Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

DABCO and DMAP – Why Are They Different in Organocatalysis?

Mahiuddin Baidya,[a] Shinjiro Kobayashi,[a] Frank Brotzel,[a] Uli Schmidhammer,[b] Eberhard Riedle,[b] and Herbert Mayr[a]*

[a] *Department Chemie und Biochemie*
Ludwig-Maximilians-Universität München
Butenandtstraße 5-13 (Haus F)
81377 München (Germany)
Fax: (+49) 89-2180-77717
E-mail: herbert.mayr@cup.uni-muenchen.de

[b] *Lehrstuhl für BioMolekulare Optik*
Ludwig-Maximilians-Universität München
Oettingenstrasse 67, 80538 München (Germany)

Determination of the Rate Constants for the Reactions of Amines with Benzhydrylium Ions

All rate constants were measured by the laser-flash photolysis technique. A solution of known concentration of benzhydrylium tetrafluoroborate in CH_3CN ($\approx 10^{-5}$ mol L^{-1}) was mixed with a known concentration of amine solution in CH_3CN ($\approx 10^{-3}$ mol L^{-1}) and the resulting colorless solution was then irradiated with 7-ns laser pulses (266 nm) to regenerate the benzhydrylium ions Ar_2CH^+. The decay of the absorbance of Ar_2CH^+ was monitored by UV/Vis spectroscopy at the corresponding absorption maxima. The resulting pseudo-first-order rate constants k_{obs} were obtained from at least five runs (typically 8–9 runs) at each amine concentration. The temperature of the solutions was kept constant at 20 °C by using a circulating bath thermostat and monitored with a thermocouple probe. The absorbance-time curves were fitted to the single exponential function, $A = A_0 \exp(-k_{obs}t) + C$ to yield the rate constants k_{obs} (s^{-1}).

The less stabilized benzhydrylium ions ($E \geq 0$) were generated from suitable precursors [Ph_2CH^+ from Ph_2CH-Cl, $(tol)_2CH^+$ from $(tol)_2CH$-Cl, and $(ani)_2CH^+$ from $(ani)_2CH$-OAc] by the laser pulse. Initial concentrations of the cation precursors are given in Tables S2 and S3. The actual carbocation concentrations are much lower than the initial precursor concentrations because each laser pulse converts only 1-4% of the precursor molecules into the corresponding carbocations.

Laser Flash Photolysis Setup

The laser pulse (7 ns pulse width, 266 nm, 40-60 mJ/pulse) originates from a Nd-YAG laser (Innolas SpitLight 600) with second (532 nm) and fourth (266 nm) harmonic generators. The UV-visible detection unit of the laser flash photolysis setup comprises a Xe-light source (Osram XBO 150 W/CR OFR in a Hamamatsu E7536 housing with Hamamatsu C8849 power supplier), a spectrograph (Acton Spectra Pro 2300i from Princeton Instruments), a photomultiplier (Hamamatsu H-7332-10 with C7169 power supply) with amplifier (Stanford Research Systems SR445A), and a pulse generator (Berkeley Nucleonics Corp. BNC 565). For the data acquisition a 350 MHz-oscilloscope (Tektronix DPO 4032) was used. The sample was kept in a temperature controlled fluorescence cell, the temperature of which was maintained at 20 °C by a circulating bath thermostat. A shutter was used to prevent the unnecessarily long exposure of the sample to the light from the Xe-lamp.

Several of the rate constants reported in this work have independently been determined using excitation of the samples with UV-Vis tunable femtosecond pulses.[S1]

Determination of the Equilibrium Constants and Intrinsic Barriers

Because benzhydrylium ions Ar_2CH^+ are colored and their reaction with colorless amines yields colorless ammonium ions, the equilibrium constants can be determined by UV-vis spectroscopy. In order to determine the equilibrium constants K, the molar absorptivities ε of the Ar_2CH^+ BF_4^- salts were determined in acetonitrile solution assuming the validity of Lambert-Beer's law. The amines were added to solutions of the carbocations and after a few seconds when the equilibrium was reached, the absorbance of the solutions were determined photometrically and

[S1] U. Schmidhammer, S. Roth, E. Riedle, A. A. Tishkov, H. Mayr, *Rev. Sci. Instrum.* **2005**, *76*, 093111.

converted into concentrations of Ar_2CH^+ using the ε values listed in Table S1. Their combination with initial concentrations of the amines yields the equilibrium constant *K*.

$$Ar_2CH^+ + NR_3 \underset{}{\overset{K}{\rightleftharpoons}} Ar_2CH\text{-}NR_3^+ \qquad (2)$$

$$K = \frac{[Ar_2CH\text{-}NR_3^+]}{[Ar_2CH^+]\ [NR_3]} = \frac{(A_0 - A)}{A\ [NR_3]} \qquad (3)$$

where $[NR_3] = [NR_3]_0 - [Ar_2CH\text{-}NR_3^+]$

and $[Ar_2CH^+] = A/(\varepsilon\ d)$ where A = absorbance, ε = molar absorption coefficient and *d* = path length.

Equilibrium constants *K* have been measured with variable concentrations at 20°C. The average of the individual experiments is given at the bottom of each table.

Materials

Commercially available acetonitrile (VWR, HPLC-gradient grade) was used without further purification for all laser flash photolysis experiments and determinations of equilibrium constants. DABCO (Acros, 97%), quinuclidine (Fluka, ≥97.0%), and DMAP (Aldrich, >99%) were used without further purification. The linear correlation between pseudo-first-order rate constants k_{obs} and concentration of amines indicates that potential reactive contaminations in the amines cannot adulterate the results. The failure to obtain constant absorbances in equilibrium experiments, where benzhydrylium ions are combined with a large excess of DABCO or quinuclidine may be due to unknown impurities, however. 4-Methoxypyridine (Aldrich, 97%), 3,4-lutidine (Acros, 98%), and 3,5-lutidine (Fluka, >97%) were freshly distilled under nitrogen before the experiments for the determination of equilibrium constants.

The benzhydrylium tetrafluoroborates $Ar_2CH^+\ BF_4^-$ were prepared as described before.[S2] Chlorodiphenylmethane (Acros, 98%) was used without further purification. The other benzhydryl acetates and chlorides were prepared according to the procedures described below. The obtained spectrosopic data are in agreement with published literature values.

For the synthesis of 4,4'-dimethoxybenzhydryl acetate,[S3] 4,4'-dimethoxybenzhydrol, (2.6 g, 10.6 mmol) was dissolved in benzene (15 mL). DMAP (0.1 equiv) and triethylamine (1.2 equiv) were added and stirred for 5 min. Then acetic anhydride (1 equiv) was added and stirring was continued for 3 h at room temperature. Subsequently, pentane (15 mL) was added, and the reaction mixture was washed quickly with 0.2 M hydrochloric acid (10 mL), followed by aq. $NaHCO_3$ (10 mL) and water. After drying ($MgSO_4$) and filtration, the solvent was evaporated under vacuum. Finally, the crude product was recrystallized twice from a Et_2O/THF mixture (1:1) diluted with *n*-pentane.

For the synthesis of 4,4'-dimethylbenzhydryl chloride,[S4] 4,4'-dimethylbenzhydrol (2.0 g, 9.4 mmol) was dissolved in dry CH_2Cl_2 (20 mL) and cooled to 0 °C. Then conc. aqueous HCl (10 mL) was added dropwise under nitrogen while keeping the temparature at 0°C. The mixture was stirred for 1 h and then extracted with dry CH_2Cl_2. After drying ($CaCl_2$) the solvent was

[S2] H. Mayr, T. Bug, M. F. Gotta, N. Hering, B. Irrgang, B. Janker, B. Kempf, R. Loos, A. R. Ofial, G. Remennikov, H. Schimmel, *J. Am. Chem. Soc.* **2001**, *123*, 9500-9512.

[S3] In analogy to a method described by: J. E. C. Miles, R. S. Ramsewak, M. G. Nair, *J. Agric. Food Chem.* **2000**, *48*, 503–506.

[S4] Modification of a procedure described in: H. Mayr, R. Pock, *Chem. Ber.* **1986**, *119*, 2473–2496.

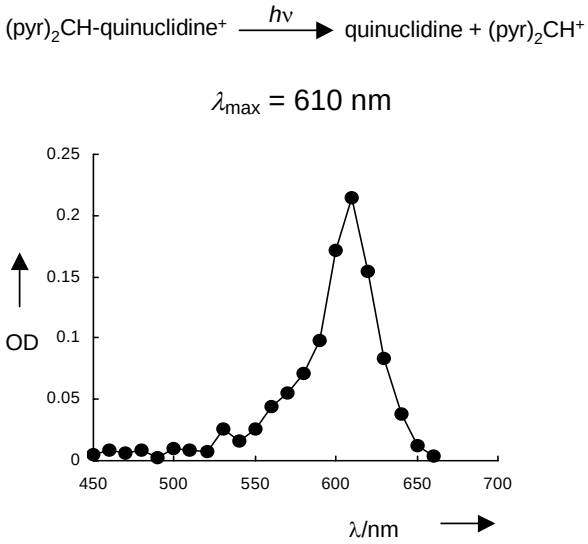
evaporated under vacuum. The crude 4,4'-dimethylbenzhydryl chloride was recrystallized from *n*-pentane.

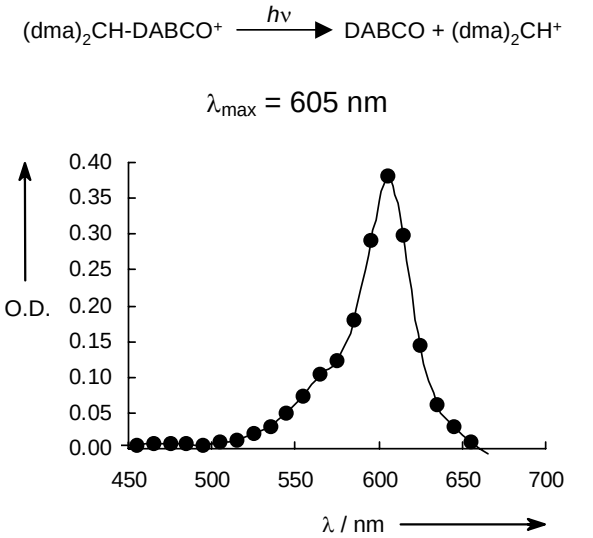
Table S1. Molar absorption coefficients ε of the benzhydrylium ions in CH_3CN.[a]

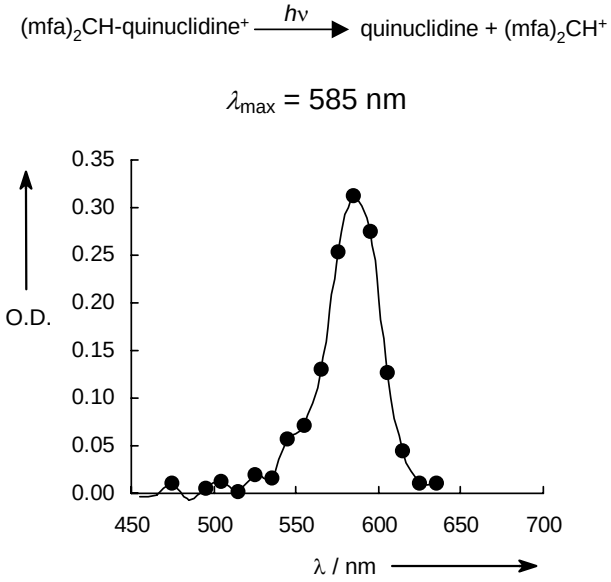
Ar_2CH^+	λ_{max} (nm)	ε (M^{-1} cm^{-1})
$(lil)_2CH^+$	632	1.317×10^5
$(jul)_2CH^+$	635	1.727×10^5
$(ind)_2CH^+$	616	1.287×10^5
$(thq)_2CH^+$	620	1.006×10^5
$(pyr)_2CH^+$	611	1.390×10^5
$(dma)_2CH^+$	605	1.464×10^5
$(mfa)_2CH^+$	586	1.592×10^5

[a] R. Loos, H. Mayr, unpublished results.

Generation of Benzhydrylium Ions from Ammonium Salts 5 by the Laser-Flash Technique







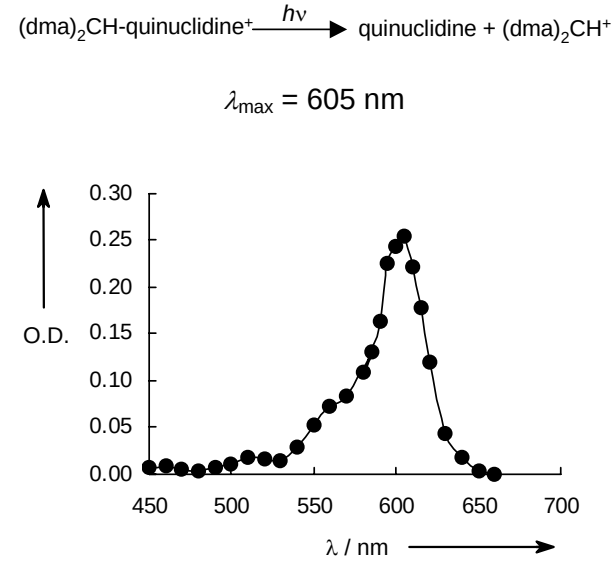


Table S2. Kinetics of the Reactions of DABCO (**1**) with Ar_2CH^+ (20°C, CH_3CN)

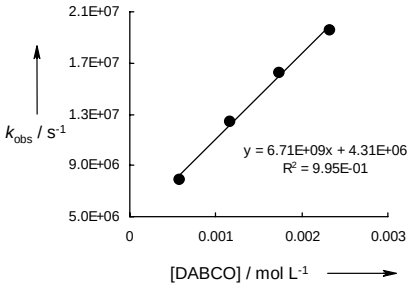
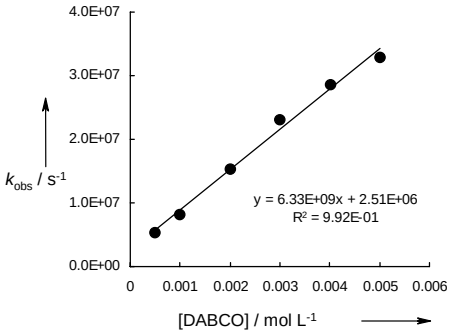
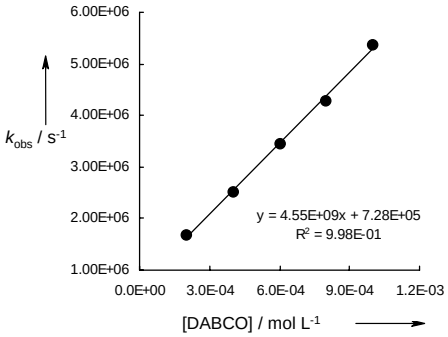
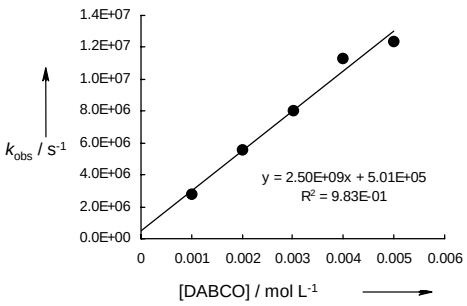
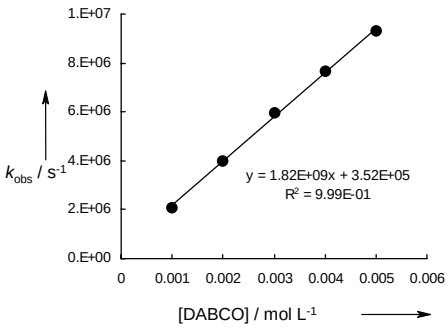
Ar_2CH^+	[DABCO] (mol L^{-1})	k_{obs} (s^{-1})		k_2 (L mol^{-1} s^{-1})
$[(Ph_2CHCl)]_0 = 1.00\times10^{-3}$ mol L^{-1}				
Ph_2CH^+	0.0006	7.88×10^6		6.71×10^9
	0.0012	1.25×10^7		
	0.0017	1.62×10^7		
	0.0023	1.96×10^7		
$[(tol)_2CHCl]_0 = 1.00\times10^{-3}$ mol L^{-1}				
$(tol)_2CH^+$	0.0005	5.28×10^6		6.33×10^9
	0.0010	8.19×10^6		
	0.0020	1.56×10^7		
	0.0030	2.14×10^7		
	0.0040	2.28×10^7		
	0.0050	3.29×10^7		
$[(ani)_2CHOAc)]_0 = 1.00\times10^{-3}$ mol L^{-1}				
$(ani)_2CH^+$	0.0002	1.68×10^6		4.55×10^9
	0.0004	2.52×10^6		
	0.0006	3.46×10^6		
	0.0008	4.28×10^6		
	0.0010	5.36×10^6		
$[(pfa)_2CH^+BF_4^-]_0 = 2.00\times10^{-5}$ mol L^{-1}				
$(pfa)_2CH^+$	0.001	2.75×10^6		2.50×10^9
	0.002	5.57×10^6		
	0.003	8.02×10^6		
	0.004	1.13×10^7		
	0.005	1.24×10^7		
$[(mfa)_2CH^+BF_4^-]_0 = 2.00\times10^{-5}$ mol L^{-1}				
$(mfa)_2CH^+$	0.001	2.07×10^6		1.82×10^9
	0.002	4.01×10^6		
	0.003	5.94×10^6		
	0.004	7.66×10^6		
	0.005	9.32×10^6		

Table S2 (continued).

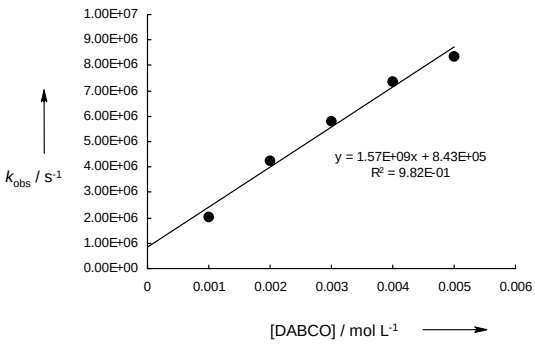
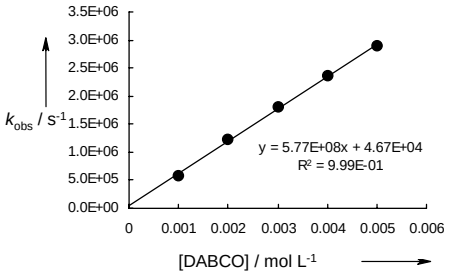
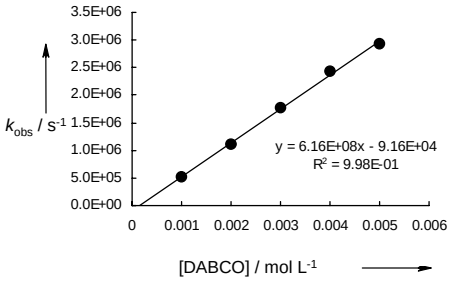
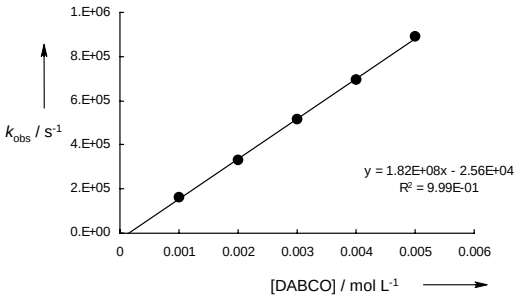
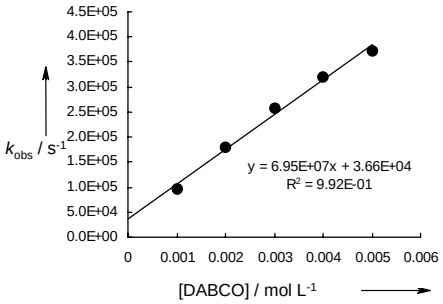
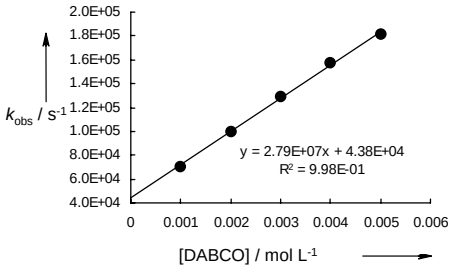
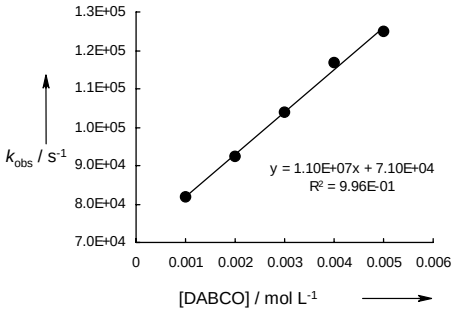
Ar_2CH^+	[DABCO] (mol L^{-1})	k_{obs} (s^{-1})		k_2 (L mol^{-1} s^{-1})
$[(dpa)_2CH^+BF_4^-]_0 = 2.00\times10^{-5}$ mol L^{-1}				
$(dpa)_2CH^+$	0.001	2.04×10^6		
	0.002	4.25×10^6		
	0.003	5.79×10^6		
	0.004	7.38×10^6		
	0.005	8.34×10^6		1.57×10^9
$[(mor)_2CH^+BF_4^-]_0 = 2.00\times10^{-5}$ mol L^{-1}				
$(mor)_2CH^+$	0.001	5.19×10^5		
	0.002	1.12×10^6		
	0.003	1.77×10^6		
	0.004	2.44×10^6		
	0.005	2.93×10^6		5.77×10^8
$[(mpa)_2CH^+BF_4^-]_0 = 2.00\times10^{-5}$ mol L^{-1}				
$(mpa)_2CH^+$	0.001	5.86×10^5		
	0.002	1.23×10^6		
	0.003	1.80×10^6		
	0.004	2.37×10^6		
	0.005	2.90×10^6		6.16×10^8
$[(dma)_2CH^+BF_4^-]_0 = 8.00\times10^{-6}$ mol L^{-1}				
$(dma)_2CH^+$	0.001	1.65×10^5		
	0.002	3.31×10^6		
	0.003	5.14×10^6		
	0.004	6.97×10^6		
	0.005	8.90×10^6		1.82×10^8
$[(pyr)_2CH^+BF_4^-]_0 = 2.00\times10^{-5}$ mol L^{-1}				
$(pyr)_2CH^+$	0.001	9.61×10^4		
	0.002	1.79×10^5		
	0.003	2.57×10^5		
	0.004	3.21×10^5		
	0.005	3.73×10^5		6.95×10^7

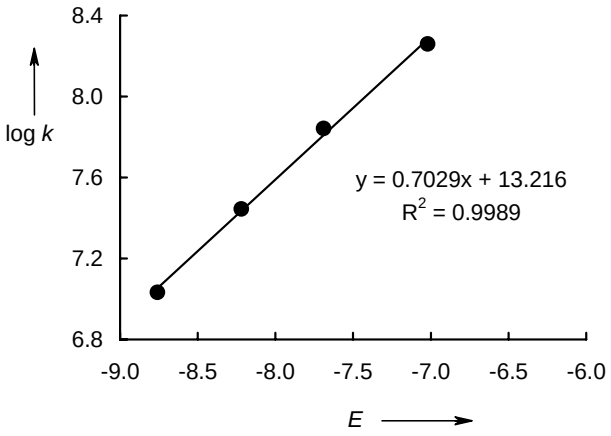
Table S2 (continued).

Ar_2CH^+	[DABCO] (mol L^{-1})	k_{obs} (s^{-1})		k_2 (L mol^{-1} s^{-1})
$[(thq)_2CH^+BF_4^-]_0 = 5.00\times10^{-5}$ mol L^{-1}				
$(thq)_2CH^+$	0.001	7.00×10^4		2.79×10^7
	0.002	1.00×10^5		
	0.003	1.29×10^5		
	0.004	1.57×10^5		
	0.005	1.81×10^5		
$[(ind)_2CH^+BF_4^-]_0 = 5.00\times10^{-5}$ mol L^{-1}				
$(ind)_2CH^+$	0.001	8.20×10^4		1.10×10^7
	0.002	9.25×10^4		
	0.003	1.04×10^5		
	0.004	1.17×10^5		
	0.005	1.25×10^5		

Determination of the Nucleophilicity Parameters *N* and *s* for DABCO (**1**) in Acetonitrile

Reactions with rate constants $k_2 > 2 \times 10^8$ L mol^{-1} s^{-1} (20 °C) have not been used for the determination of the reactivity parameters *N* and *s*.

Ar_2CH^+	*E*	k_2 (L mol^{-1} s^{-1})	log *k*
$(ind)_2CH^+$	–8.76	1.10×10^7	7.04
$(thq)_2CH^+$	–8.22	2.79×10^7	7.45
$(pyr)_2CH^+$	–7.69	6.95×10^7	7.84
$(dma)_2CH^+$	–7.02	1.82×10^8	8.26



Nucleophilicity parameters for **DABCO (in MeCN): *N* = 18.80, *s* = 0.703**

Table S3. Kinetics of the Reactions of Quinuclidine (**2**) with Ar_2CH^+ (20°C, CH_3CN)

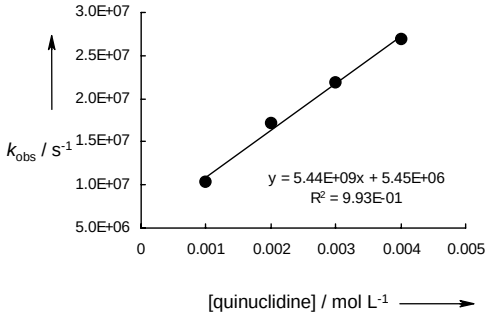
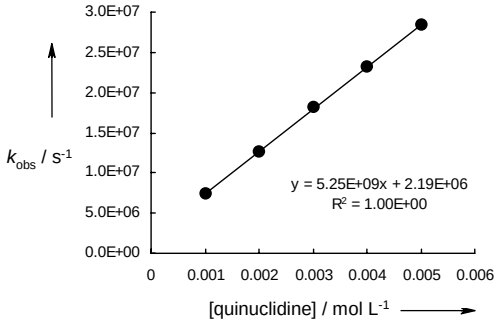
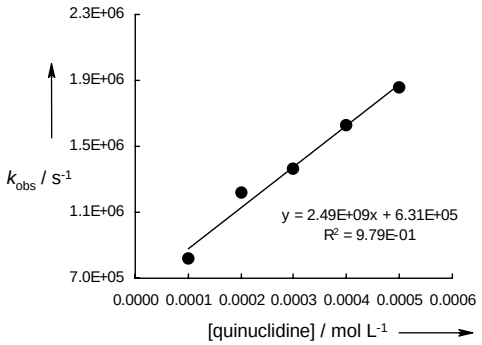
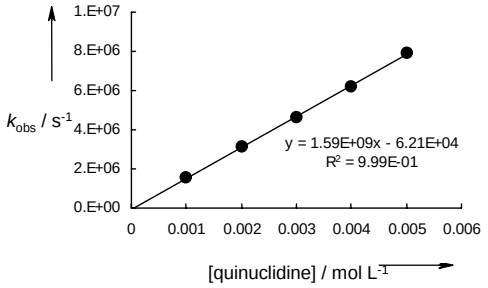
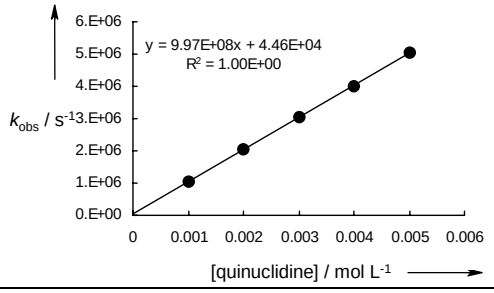
Ar_2CH^+	[quinuclidine] (mol L^{-1})	k_{obs} (s^{-1})		k_2 (L mol^{-1} s^{-1})
$[Ph_2CHCl]_0 = 1.00 \times 10^{-3}$ mol L^{-1}				
Ph_2CH^+	0.001	1.03×10^7		5.44×10^9
	0.002	1.71×10^7		
	0.003	2.19×10^7		
	0.004	2.69×10^7		
$[(tol)_2CHCl]_0 = 1.00 \times 10^{-3}$ mol L^{-1}				
$(tol)_2CH^+$	0.001	7.41×10^6		5.25×10^9
	0.002	1.26×10^7		
	0.003	1.81×10^7		
	0.004	2.32×10^7		
	0.005	2.84×10^7		
$[(ani)_2CHOAc]_0 = 1.00 \times 10^{-3}$ mol L^{-1}				
$(ani)_2CH^+$	0.0001	8.15×10^5		2.49×10^9
	0.0002	1.22×10^6		
	0.0003	1.37×10^6		
	0.0004	1.63×10^6		
	0.0005	1.85×10^6		
$[(pfa)_2CH^+BF_4^-]_0 = 2.00 \times 10^{-5}$ mol L^{-1}				
$(pfa)_2CH^+$	0.001	1.56×10^6		1.59×10^9
	0.002	3.12×10^6		
	0.003	4.63×10^6		
	0.004	6.23×10^6		
	0.005	7.93×10^6		
$[(mfa)_2CH^+BF_4^-]_0 = 2.00 \times 10^{-5}$ mol L^{-1}				
$(mfa)_2CH^+$	0.001	1.03×10^6		9.97×10^8
	0.002	2.06×10^6		
	0.003	3.05×10^6		
	0.004	3.98×10^6		
	0.005	5.05×10^6		

Table S3 (continued).

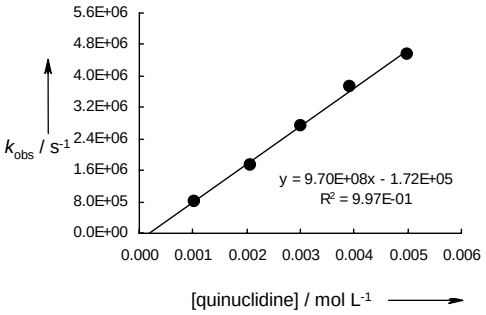
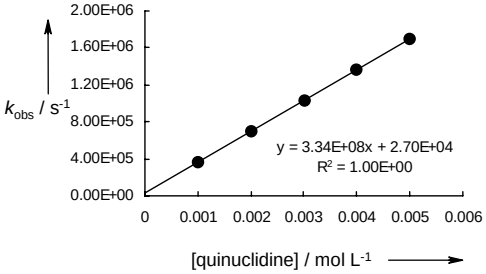
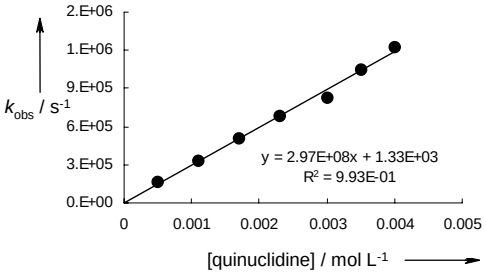
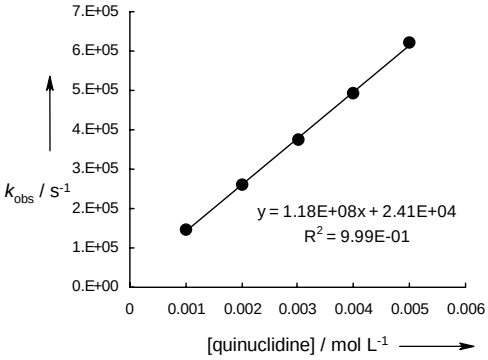
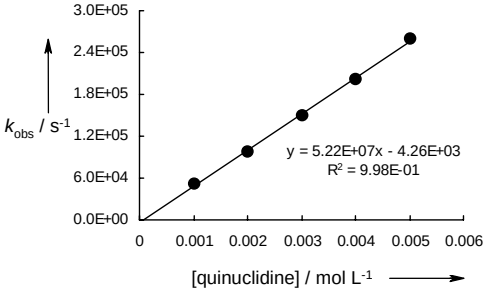
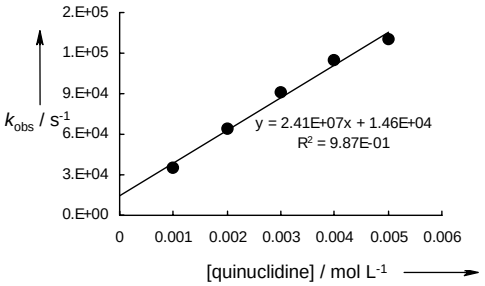
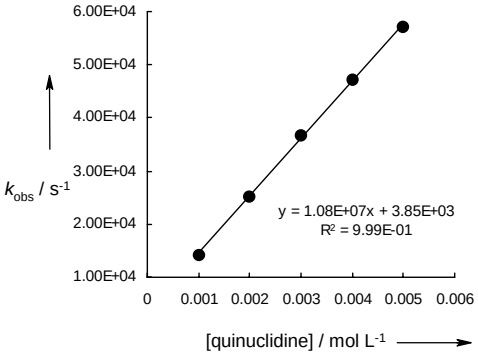
Ar_2CH^+	[quinuclidine] (mol L^{-1})	k_{obs} (s^{-1})		k_2 (L mol^{-1} s^{-1})
$[(dpa)_2CH^+BF_4^-]_0 = 2.00 \times 10^{-5}$ mol L^{-1}				
$(dpa)_2CH^+$	0.001	8.36×10^5		9.70×10^8
	0.002	1.75×10^6		
	0.003	2.75×10^6		
	0.004	3.76×10^6		
	0.005	4.57×10^6		
$[(mor)_2CH^+BF_4^-]_0 = 2.00 \times 10^{-5}$ mol L^{-1}				
$(mor)_2CH^+$	0.001	3.60×10^5		3.34×10^8
	0.002	6.92×10^5		
	0.003	1.04×10^6		
	0.004	1.37×10^6		
	0.005	1.69×10^6		
$[(mpa)_2CH^+BF_4^-]_0 = 2.00 \times 10^{-5}$ mol L^{-1}				
$(mpa)_2CH^+$	0.0005	1.66×10^5		2.97×10^8
	0.0011	3.28×10^5		
	0.0017	5.10×10^5		
	0.0023	6.80×10^5		
	0.0030	8.25×10^5		
	0.0035	1.05×10^6		
	0.0040	1.23×10^6		
$[(dma)_2CH^+BF_4^-]_0 = 8.00 \times 10^{-6}$ mol L^{-1}				
$(dma)_2CH^+$	0.001	1.47×10^5		1.18×10^8
	0.002	2.60×10^5		
	0.003	3.74×10^5		
	0.004	4.93×10^5		
	0.005	6.21×10^5		
$[(pyr)_2CH^+BF_4^-]_0 = 2.00 \times 10^{-5}$ mol L^{-1}				
$(pyr)_2CH^+$	0.001	5.18×10^4		5.22×10^7
	0.002	9.77×10^4		
	0.003	1.49×10^5		
	0.004	2.02×10^5		
	0.005	2.60×10^5		

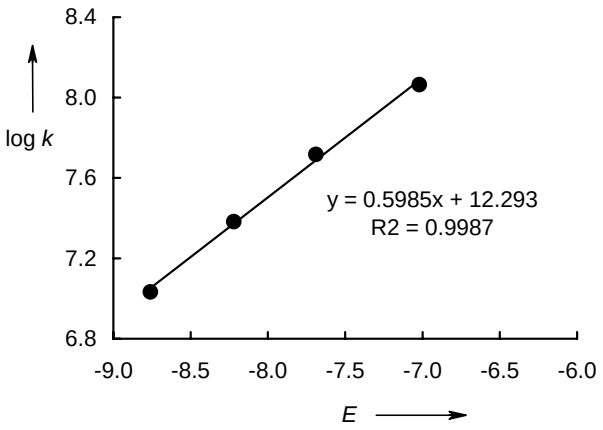
Table S3 (continued).

Ar_2CH^+	[quinuclidine] (mol L^{-1})	k_{obs} (s^{-1})		k_2 (L mol^{-1} s^{-1})
$[(thq)_2CH^+BF_4^-]_0 = 5.00 \times 10^{-5}$ mol L^{-1}				
$(thq)_2CH^+$	0.001	3.48×10^4		2.41×10^7
	0.002	6.40×10^4		
	0.003	9.06×10^4		
	0.004	1.15×10^5		
	0.005	1.30×10^5		
$[(ind)_2CH^+BF_4^-]_0 = 5.00 \times 10^{-5}$ mol L^{-1}				
$(ind)_2CH^+$	0.001	1.42×10^4		1.08×10^7
	0.002	2.53×10^4		
	0.003	3.68×10^4		
	0.004	4.71×10^4		
	0.005	5.71×10^4		

Determination of the Nucleophilicity Parameters *N* and *s* for Quinuclidine (**2**) in Acetonitrile

Reactions with rate constants $k_2 > 2 \times 10^8$ L mol^{-1} s^{-1} (20 °C) have not been used for the determination of the reactivity parameters *N* and *s*.

Ar_2CH^+	*E*	k_2 (L mol^{-1} s^{-1})	log *k*
$(ind)_2CH^+$	–8.76	1.08×10^7	7.03
$(thq)_2CH^+$	–8.22	2.41×10^7	7.38
$(pyr)_2CH^+$	–7.69	5.22×10^7	7.72
$(dma)_2CH^+$	–7.02	1.18×10^8	8.07



Nucleophilicity parameters for **Quinuclidine (in MeCN): *N* = 20.54, *s* = 0.598**

Equilibrium Constants for the Reactions of Amines with Ar_2CH^+ BF_4^-

All equilibrium measurements have been performed at 20 °C in acetonitrile.

Equilibrium constant for the reaction of $(lil)_2CH^+BF_4^-$ and DMAP
ε [$(lil)_2CH^+$ at 632 nm] = 1.317 × 10^5 M^{-1} cm^{-1} and d = 0.5 cm

Entry	$[DMAP]_0$ (mol L^{-1})	A	$[(lil)_2CH^+]_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.734	1.114E-05	
1	2.868E-05	0.460	6.984E-06	2.43E+04
2	5.713E-05	0.329	4.997E-06	2.41E+04
3	8.536E-05	0.253	3.846E-06	2.43E+04
4	1.134E-04	0.206	3.133E-06	2.43E+04
0	0	0.733	1.113E-05	
1	2.868E-05	0.461	6.999E-06	2.41E+04
2	5.713E-05	0.326	4.949E-06	2.45E+04
3	8.536E-05	0.253	3.845E-06	2.43E+04
4	1.134E-04	0.205	3.111E-06	2.45E+04
0	0	0.736	1.117E-05	
1	2.868E-05	0.460	6.976E-06	2.45E+04
2	5.713E-05	0.327	4.965E-06	2.45E+04
3	8.536E-05	0.252	3.824E-06	2.46E+04
4	1.134E-04	0.206	3.127E-06	2.44E+04

K_{av}(20 °C) = 2.44 × 10^4 L mol^{-1}

Equilibrium constant for the reaction of $(jul)_2CH^+$ BF_4^- and DMAP
ε [$(jul)_2CH^+$ at 635 nm] = 1.727 × 10^5 M^{-1} cm^{-1} and d = 0.5 cm

Entry	$[DMAP]_0$ (mol L^{-1})	A	$[(jul)_2CH^+]_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.644	7.458E-06	
1	2.865E-05	0.389	4.505E-06	2.551E+04
2	5.708E-05	0.270	3.127E-06	2.626E+04
3	8.527E-05	0.205	2.377E-06	2.665E+04
0	0	0.652	7.555E-06	
1	2.865E-05	0.393	4.554E-06	2.568E+04
2	5.708E-05	0.276	3.196E-06	2.587E+04
3	8.527E-05	0.214	2.472E-06	2.564E+04
4	1.132E-04	0.172	1.992E-06	2.594E+04
0	0	0.654	7.573E-06	
1	2.865E-05	0.393	4.554E-06	2.586E+04
2	5.708E-05	0.277	3.208E-06	2.582E+04
3	8.527E-05	0.212	2.455E-06	2.601E+04
4	1.132E-04	0.171	1.980E-06	2.624E+04
0	0	0.656	7.597E-06	
1	2.865E-05	0.396	4.586E-06	2.560E+04
2	5.708E-05	0.278	3.219E-06	2.580E+04
3	8.527E-05	0.213	2.467E-06	2.595E+04
4	1.132E-04	0.168	1.945E-06	2.700E+04

K_{av}(20 °C) = 2.60 × 10^4 L mol^{-1}

Equilibrium constant for the reaction of $(ind)_2CH^+$ BF_4^- and DMAP

ε [$(ind)_2CH^+$ at 616 nm] = 1.287×10^5 M^{-1} cm^{-1} and d = 0.5 cm

Entry	$[DMAP]_0$ (mol L^{-1})	A	$[(ind)_2CH^+]_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.889	1.382E-05	
1	1.430E-05	0.252	3.923E-06	5.73E+05
2	2.854E-05	0.091	1.421E-06	5.40E+05
0	0	0.892	1.386E-05	
1	1.437E-05	0.251	3.900E-06	5.79E+05
2	2.868E-05	0.092	1.425E-06	5.37E+05
0	0	0.895	1.391E-05	
1	1.437E-05	0.251	3.900E-06	5.88E+05
2	2.868E-05	0.091	1.418E-06	5.44E+05

K_{av}(20 °C) = 5.60×10^5 L mol^{-1}

Equilibrium constant for the reaction of $(pyr)_2CH^+$ BF_4^- and quinuclidine

ε [$(pyr)_2CH^+$ at 611 nm] = 1.390×10^5 $M^{-1}cm^{-1}$ and d = 0.5 cm

Entry	$[amine]_0$ (mol L^{-1})	A	$[(pyr)_2CH^+]_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.480	6.911E-06	
1	5.068E-05	0.151	2.171E-06	4.75E+04
2	7.594E-05	0.113	1.629E-06	4.59E+04
3	1.012E-04	0.087	1.255E-06	4.72E+04
4	1.263E-04	0.076	1.089E-06	4.44E+04
0	0	0.492	7.079E-06	
1	2.604E-05	0.246	3.533E-06	4.46E+04
2	5.203E-05	0.160	2.300E-06	4.40E+04
3	7.796E-05	0.117	1.684E-06	4.41E+04
4	1.038E-04	0.092	1.321E-06	4.44E+04
5	1.297E-04	0.076	1.097E-06	4.41E+04
0	0	0.484	6.966E-06	
1	5.175E-05	0.161	2.316E-06	4.26E+04
2	7.755E-05	0.116	1.675E-06	4.37E+04
3	1.033E-04	0.088	1.267E-06	4.61E+04
4	1.290E-04	0.075	1.072E-06	4.47E+04

K_{av}(20 °C) = 4.49×10^4 L mol^{-1}

Equilibrium constant for the reaction of $(thq)_2CH^+$ BF_4^- and quinuclidine

ε [$(thq)_2CH^+$ at 620 nm] = 1.006×10^5 M^{-1} cm^{-1} and d = 0.5 cm

Entry	$[amine]_0$ (mol L^{-1})	A	$[(thq)_2CH^+]_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.131	2.613E-06	
1	5.127E-05	0.070	1.396E-06	1.74E+04
2	1.023E-04	0.050	9.872E-07	1.63E+04
3	1.532E-04	0.039	7.712E-07	1.58E+04
4	2.038E-04	0.030	5.987E-07	1.67E+04
5	2.543E-04	0.025	4.971E-07	1.69E+04
0	0	0.129	2.561E-06	
1	5.100E-05	0.067	1.338E-06	1.84E+04
2	1.018E-04	0.049	9.737E-07	1.63E+04
3	1.524E-04	0.037	7.387E-07	1.64E+04
4	2.028E-04	0.030	5.908E-07	1.66E+04
5	2.529E-04	0.024	4.847E-07	1.71E+04

K_{av}(20 °C) = 1.68×10^4 L mol^{-1}

Equilibrium constant for the reaction of $(pyr)_2CH^+$ BF_4^- and DABCO

ε [$(pyr)_2CH^+$ at 611 nm] = 1.390 × 10^5 M^{-1} cm^{-1} and d = 0.5 cm

Entry	$[DABCO]_0$ (mol L^{-1})	A	$[(pyr)_2CH^+]_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.964	1.387E-05	
1	3.635E-04	0.346	4.977E-06	5.04E+03
2	4.521E-04	0.302	4.337E-06	4.97E+03
3	5.392E-04	0.271	3.898E-06	4.83E+03
4	6.247E-04	0.246	3.544E-06	4.74E+03
5	7.082E-04	0.224	3.222E-06	4.74E+03
6	7.897E-04	0.206	2.963E-06	4.72E+03
7	8.689E-04	0.189	2.722E-06	4.77E+03
8	9.456E-04	0.174	2.506E-06	4.85E+03
9	1.020E-03	0.163	2.349E-06	4.86E+03
10	1.091E-03	0.153	2.205E-06	4.90E+03
11	1.160E-03	0.144	2.071E-06	4.96E+03
12	1.226E-03	0.129	1.860E-06	5.32E+03

K_{av}(20 °C) = 4.89 × 10^3 L mol^{-1}

Equilibrium constant for the reaction of $(thq)_2CH^+$ BF_4^- and DABCO

ε [$(thq)_2CH^+$ at 620 nm] = 1.006 × 10^5 M^{-1} cm^{-1} and d = 0.5 cm

Entry	$[DABCO]_0$ (mol L^{-1})	A	$[(thq)_2CH^+]_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.157	3.118E-06	
1	8.431E-05	0.138	2.736E-06	1.66E+03
2	1.683E-04	0.128	2.545E-06	1.34E+03
3	2.516E-04	0.118	2.346E-06	1.31E+03
4	3.341E-04	0.102	2.028E-06	1.61E+03
5	4.156E-04	0.090	1.789E-06	1.79E+03
6	5.777E-04	0.083	1.650E-06	1.54E+03
0	0	0.153	3.040E-06	
1	1.667E-04	0.123	2.436E-06	1.49E+03
2	3.321E-04	0.098	1.949E-06	1.69E+03
3	4.951E-04	0.085	1.690E-06	1.62E+03
4	6.548E-04	0.076	1.511E-06	1.55E+03

K_{av}(20 °C) = 1.56 × 10^3 L mol^{-1}

Equilibrium constant for the reaction of $(ind)_2CH^+$ BF_4^- and (4-methoxy)pyridine

ε [$(ind)_2CH^+$ at 616 nm] = 1.287 × 10^5 M^{-1} cm^{-1} and d = 0.5 cm

Entry	$[amine]_0$ (mol L^{-1})	A	$[(ind)_2CH^+]_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.896	1.392E-05	
1	1.379E-03	0.810	1.259E-05	7.67E+01
2	2.340E-03	0.761	1.182E-05	7.56E+01
3	3.283E-03	0.723	1.123E-05	7.27E+01
4	4.207E-03	0.685	1.064E-05	7.32E+01
0	0	0.904	1.405E-05	
1	2.475E-03	0.774	1.203E-05	6.77E+01
2	4.900E-03	0.682	1.060E-05	6.63E+01
3	7.278E-03	0.609	9.469E-06	6.64E+01
4	9.609E-03	0.550	8.538E-06	6.71E+01
5	1.190E-02	0.500	7.762E-06	6.81E+01
6	1.414E-02	0.459	7.136E-06	6.85E+01
7	1.634E-02	0.422	6.563E-06	6.98E+01

K_{av}(20 °C) = 70.2 L mol^{-1}

Equilibrium constant for the reaction of $(thq)_2CH^+$ BF_4^- and (4-methoxy)pyridine

ε [$(thq)_2CH^+$ at 620 nm] = 1.006×10^5 M^{-1} cm^{-1} and d = 0.5 cm

Entry	$[amine]_0$ (mol L^{-1})	A	$[(ind)_2CH^+]_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.421	8.369E-06	
1	9.879E-04	0.371	7.386E-06	1.35E+02
2	1.956E-03	0.336	6.673E-06	1.30E+02
3	2.905E-03	0.306	6.079E-06	1.30E+02
4	3.836E-03	0.281	5.582E-06	1.30E+02
5	4.749E-03	0.259	5.156E-06	1.31E+02
6	5.645E-03	0.240	4.778E-06	1.33E+02
7	6.523E-03	0.226	4.485E-06	1.33E+02
0	0	0.416	8.269E-06	
1	9.829E-04	0.369	7.336E-06	1.29E+02
2	1.946E-03	0.334	6.633E-06	1.27E+02
3	2.891E-03	0.302	6.007E-06	1.30E+02
4	3.817E-03	0.276	5.482E-06	1.33E+02
5	4.726E-03	0.255	5.070E-06	1.34E+02
0	0	0.416	8.265E-06	
1	9.879E-04	0.369	7.337E-06	1.28E+02
2	1.956E-03	0.331	6.579E-06	1.31E+02
3	2.905E-03	0.301	5.985E-06	1.31E+02
4	3.836E-03	0.277	5.506E-06	1.31E+02
5	4.749E-03	0.255	5.062E-06	1.33E+02

K_{av}(20 °C) = 131 L mol^{-1}

Equilibrium constant for the reaction of $(pyr)_2CH^+$ BF_4^- and (4-methoxy)pyridine

ε [$(pyr)_2CH^+$ at 611 nm] = 1.390×10^5 M^{-1} cm^{-1} and d = 0.5 cm

Entry	$[amine]_0$ (mol L^{-1})	A	$[(pyr)_2CH^+]_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.748	1.076E-05	
1	4.128E-04	0.647	9.312E-06	3.78E+02
2	1.228E-03	0.516	7.425E-06	3.67E+02
3	2.030E-03	0.429	6.171E-06	3.67E+02
4	2.819E-03	0.366	5.271E-06	3.70E+02
5	3.595E-03	0.318	4.577E-06	3.76E+02
0	0	0.723	1.040E-05	
1	8.009E-04	0.560	8.053E-06	3.64E+02
2	1.589E-03	0.459	6.608E-06	3.62E+02
3	2.364E-03	0.388	5.583E-06	3.65E+02
4	3.127E-03	0.336	4.831E-06	3.69E+02
5	3.878E-03	0.296	4.257E-06	3.73E+02
0	0	0.727	1.046E-05	
1	8.009E-04	0.562	8.087E-06	3.68E+02
2	1.589E-03	0.460	6.622E-06	3.66E+02
3	2.364E-03	0.389	5.590E-06	3.69E+02
4	3.127E-03	0.336	4.827E-06	3.74E+02
5	3.878E-03	0.297	4.266E-06	3.75E+02

K_{av}(20 °C) = 370 L mol^{-1}

Equilibrium constant for the reaction of $(ind)_2CH^+$ BF_4^- and 3,4-lutidine

ε [$(ind)_2CH^+$ at 616 nm] = 1.287×10^5 M^{-1} cm^{-1} and d = 0.5 cm

Entry	$[amine]_0$ (mol L^{-1})	A	$[(ind)_2CH^+]_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.685	1.064E-05	
1	1.791E-03	0.628	9.750E-06	5.12E+01
2	5.329E-03	0.546	8.484E-06	4.78E+01
3	8.812E-03	0.484	7.520E-06	4.71E+01
4	1.224E-02	0.435	6.759E-06	4.70E+01
5	1.561E-02	0.397	6.161E-06	4.66E+01
6	1.893E-02	0.364	5.648E-06	4.67E+01
7	2.220E-02	0.331	5.149E-06	4.81E+01
8	2.542E-02	0.305	4.739E-06	4.90E+01
0	0	0.684	1.063E-05	
1	4.450E-03	0.560	8.698E-06	4.98E+01
2	8.812E-03	0.477	7.415E-06	4.91E+01
3	1.309E-02	0.417	6.479E-06	4.89E+01
4	1.728E-02	0.371	5.764E-06	4.88E+01
5	2.139E-02	0.332	5.161E-06	4.95E+01
6	2.542E-02	0.302	4.692E-06	4.98E+01
7	2.938E-02	0.276	4.295E-06	5.02E+01

K_{av}(20 °C) = 48.6 L mol^{-1}

Equilibrium constant for the reaction of $(thq)_2CH^+$ BF_4^- and 3,4-lutidine

ε [$(thq)_2CH^+$ at 620 nm] = 1.006×10^5 M^{-1} cm^{-1} and d = 0.5 cm

Entry	$[amine]_0$ (mol L^{-1})	A	$[(thq)_2CH^+]_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.347	6.908E-06	
1	4.455E-03	0.257	5.104E-06	7.93E+01
2	8.821E-03	0.203	4.035E-06	8.07E+01
3	1.310E-02	0.169	3.351E-06	8.10E+01
4	1.730E-02	0.144	2.866E-06	8.16E+01
5	2.141E-02	0.126	2.501E-06	8.23E+01
0	0	0.347	6.895E-06	
1	4.478E-03	0.257	5.103E-06	7.84E+01
2	8.866E-03	0.203	4.044E-06	7.96E+01
3	1.317E-02	0.167	3.321E-06	8.18E+01
4	1.738E-02	0.146	2.899E-06	7.93E+01
5	2.152E-02	0.130	2.585E-06	7.75E+01
0	0	0.345	6.860E-06	
1	4.455E-03	0.254	5.050E-06	8.05E+01
2	8.821E-03	0.201	4.000E-06	8.10E+01
3	1.310E-02	0.167	3.319E-06	8.14E+01
4	1.730E-02	0.143	2.845E-06	8.16E+01
5	2.141E-02	0.125	2.487E-06	8.21E+01

K_{av}(20 °C) = 80.5 L mol^{-1}

Equilibrium constant for the reaction of $(thq)_2CH^+$ BF_4^- and 3,5-lutidine

ε [$(thq)_2CH^+$ at 620 nm] = 1.006×10^5 M^{-1} cm^{-1} and d = 0.5 cm

Entry	$[amine]_0$ (mol L^{-1})	A	$[(thq)_2CH^+]_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.330	6.561E-06	
1	4.360E-03	0.292	5.796E-06	3.03E+01
2	8.634E-03	0.261	5.189E-06	3.06E+01
3	1.282E-02	0.237	4.702E-06	3.08E+01
4	1.693E-02	0.216	4.295E-06	3.12E+01
0	0	0.473	9.397E-06	
1	8.548E-03	0.380	7.555E-06	2.85E+01
2	1.677E-02	0.318	6.313E-06	2.91E+01
3	2.468E-02	0.273	5.418E-06	2.98E+01
4	3.231E-02	0.238	4.732E-06	3.05E+01
5	3.965E-02	0.212	4.215E-06	3.10E+01
0	0	0.461	9.166E-06	
1	8.548E-03	0.368	7.314E-06	2.96E+01
2	1.677E-02	0.307	6.104E-06	2.99E+01
3	2.468E-02	0.265	5.269E-06	3.00E+01
4	3.231E-02	0.230	4.573E-06	3.11E+01

K_{av}(20 °C) = 30.2 L mol^{-1}

Equilibrium constant for the reaction of $(pyr)_2CH^+$ BF_4^- and 3,5-lutidine

ε [$(pyr)_2CH^+$ at 611 nm] = 1.390×10^5 M^{-1} cm^{-1} and d = 0.5 cm

Entry	$[amine]_0$ (mol L^{-1})	A	$[(pyr)_2CH^+]_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.675	9.715E-06	
1	5.283E-04	0.643	9.252E-06	9.464E+01
2	1.395E-03	0.597	8.582E-06	9.475E+01
3	2.244E-03	0.556	8.000E-06	9.556E+01
4	3.077E-03	0.523	7.517E-06	9.510E+01
5	3.894E-03	0.492	7.082E-06	9.555E+01
6	4.696E-03	0.465	6.696E-06	9.609E+01
7	5.482E-03	0.440	6.336E-06	9.732E+01
8	6.253E-03	0.419	6.027E-06	9.789E+01
0	0	0.680	9.785E-06	
1	8.860E-04	0.629	9.041E-06	9.285E+01
2	1.754E-03	0.584	8.400E-06	9.406E+01
3	2.605E-03	0.547	7.861E-06	9.396E+01
4	3.440E-03	0.514	7.394E-06	9.406E+01

K_{av}(20 °C) = 95.2 L mol^{-1}