solutions. The unusual large magnitudes of μ_s and μ_s/μ_0 for NMA in CCl$_4$ can be traced to the absence of electrostatic interaction, causing the maximum polarization and orienting the NMA dipoles in such a fashion as to yield largest μ in this solvent.

On the other hand, the presence of —NH group in NMA appears to be responsible for (i) —CONH ....dioxane, CCl$_4$ and benzene interactions and (ii) —CONH....OCNH— intermolecular hydrogen bonding, causing dimerization with increase of concentration, depending upon the availability of electrons in these solvents. The linear plots in dioxane points to strong —CONH....dioxane interaction than —CONH....OCNH— hydrogen bonding. The smooth curves of NMA in benzene and carbon tetrachloride points to dimerization of NMA as the concentration increases. The observed behaviour can be interpreted on the basis of (—CONH....)$_{free}$ and bonded equilibrium, i.e., (—CONH....) $\rightleftharpoons$ ....(—CONH....OCNH)$_{bonded}$ from lower to higher concentration of NMA. This is supported by cryoscopic and infrared spectra. However, this peculiarity is found to be absent in a non-hydrogen bonded amide like DMA because of the absence of amino hydrogen for booding to oxygen of neighbouring molecules or to interact with solvent molecules, The overall behaviour can be represented as shown in Chart 1.
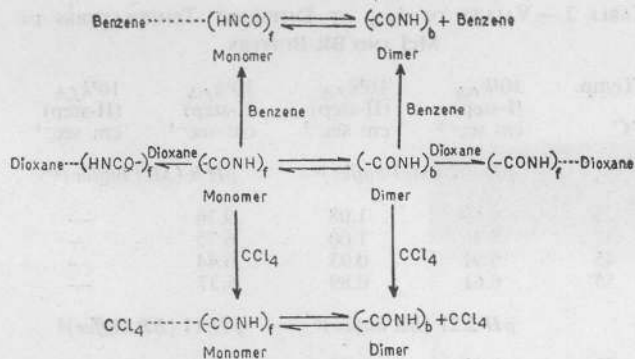

Chart 1

The infrared spectra show free ν NH at 3470 cm^{-1} in solution of concentration $< 0.01M$. The intensity of νNH decreases with increasing concentration and finally vanishes in 0.1M solution resulting in a simaltaneous shift νCO from 1690 to 1680 cm^{-1}, which is found to be absent in DMA on account of the absence of —NH group.

Further, the degree of association and observed molecular weight have been found to increase with increase in concentration of NMA as compared to almost constant molecular weight for DMA.

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Polarographic Reduction of Nitrobenzene at Different Temperatures

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The polarographic behaviour of nitrobenzene (in 25% of ethanolic solution) has been studied in McIlvaine (McI) buffers of pH 3.2 and 8 and Britton-Robinson (BR) buffers of pH 2.21 and 11 at different temperatures (25-55°). The reduction of nitrobenzene at d.m.e. is found to be irreversible and diffusion-controlled at different temperatures. The variation of kinetic parameters with temperatures suggests that the irreversible electrode reaction of nitrobenzene becomes more so at elevated temperatures.

UNLIKE inorganic depoarizers, the effect of temperature on the electrode kinetics of the irreversible reduction of organic depolarizers has not attracted much attention. Kuznetsova[1] investigated the effect of temperature on the reduction of organic depolarizers at d.m.e. and found the temperature coefficient of i_d lying between 1.15 and 1.5% per degree. Gupta and Kishore[2] reported that with increasing temperature 'αn_a' for nitrobenzene decreased while $k^0_{f,h}$ value indicated that the system was less irreversible at increasing temperature. However this observation is self-contradictory since a decrease in αn_a values signifies[3-6] that the system is tending to become more irreversible. It was therefore thought worthwhile to study the polarographic reduction of nitrobenzene at different temperatures in the range 25° to 55° in McIlvane (McI) and Britton-Robinson (BR) buffers.

All the chemicals used were either of AR or GR grade. Nitrobenzene was dissolved in 25% ethanolic solution so as to give a concentration of 1.0×10^{-3} M. Triton X-100 ($1.6 \times 10^{-5}\%$) was used as a maximum suppressor. The polarograms of deaerated solution were obtained on a manual polarograph (Toshniwal CLO2) in conjunction with a polyflex galvanometer (Toshiniwal PL50). The potentials were measured against a saturated calomel electrode (SCE). The d.m.e. had the following characteristics (in $0.1M$ KCl open circuit at 25°) : $h_{corr.} = 73.12$ cm; $t = 3.60$ sec; $m^{2/3}t^{1/6} = 2.67$ mg$^{2/3}$ sec$^{-1/2}$

The number of electrons (n) involved in the reduction process was determined by millicoulometric method of De Vries and Kroon[7] using a mercury pool cathode. Ilkovic equation was used to calculate the value of the diffusion coefficient (D) of nitrobenzene at different temperatures. The potential dependent rate constant $k_{f,h}$ was calculated by Koutecky method[8,9] and the parameters αn_a and $k^\circ_{f,h}$ from log $k_{f,h}$ versus $E_{d.e.}$ plots[10].

Nitrobenzene gives well-defined waves at different temperatures in McI and BR buffers of different pH values. In both the buffers in acidic range the reduction of nitrobenzene takes place in two steps involving 4 and 2 electrons respectively whereas in the alkaline range the reduction takes place in a single step involving 4 electrons. These observations are in agreement with those reported in the literature[11]. The two steps are diffusion-controlled at all temperatures as evidenced by the linearity of the plots of i_d versus $h^{1/2}_{corr}$ It has been found that the reduction of nitrobenzene in both the steps takes place irreversibly[12a-15].

It has been observed that $E_{1/2}$ values of both the steps are shifted to more negative potentials with rise in temperature. The temperature coefficient of i_d of both the steps lies between + 1.0% to + 2.0% per degree. This is in agreement with the values predicted by Meites[12b] for organic molecules.

A perusal of Table 1 reveals that the product αn_a registers a decrease as the temperature is raised from 25° to 55°. Vijaylakshamma and Subrahamanya[16] have shown the value of n_a to be equal to 2. Since the decrease in αn_a values with increasing temperature is indiscrete and at no stage the two consecutive values vary by a factor of 2, the possibility of decrease in the value of product αn_a due to a change in n_a may be ruled out.

Thus it may be concluded that it is α which is decreasing. A decrease in the value of α implies that the transfer of electron/eletcrons is made increasingly difficult as the temperature is elevated. In ohter words the electrode reaction of nitrobenzene in both the buffers is rendered increasingly more irreversible. The shift in $E_{1/2}$ values to more negative potentials lends support to the above conclusion.

The $k^\circ_{f,h}$ values do not show any regularity with increase in temperature. Meites[12c] has also hinted at the limitation of $k_{f,h}$ in interpreting the results. As a matter of fact it is the $k_{s,h}$ (the standard rate constant) the value of which determines the extent of irreversibility of a certain electrode reaction. Unfortunately $k_{s,h}$ could not be determined in the present study as it is not possible to know the value of standard electrode potential for nitrobenzene. However the influence of temperature on the rate of

TABLE 1 — VALUES OF KINETIC PARAMETERS AT DIFFERENT TEMPERATURES IN McI AND BR BUFFERS OF DIFFERENT pH VALUES

Temp. °C	I step		II step	
	αn_a	$k^\circ_{f,h}$ cm/sec.	αn_a	$k_{f,h}$ cm/sec.
		McI buffer pH 3.2		
25	0.68	7.78×10^{-5}	0.54	1.48×10^{-9}
35	0.63	6.60×10^{-5}	0.45	1.30×10^{-8}
45	0.61	6.86×10^{-4}	0.38	7.7×10^{-8}
55	0.60	6.61×10^{-5}	0.36	7.90×10^{-8}
		McI buffer, pH 8		
25	0.94	3.61×10^{-10}	—	—
35	0.77	4.03×10^{-9}	—	—
45	0.70	1.34×10^{-8}	—	—
55	0.68	1.70×10^{-8}	—	—
		BR buffer pH 2.21		
25	0.88	9.82×10^{-4}	0.42	2.55×10^{-6}
35	0.80	1.46×10^{-5}	0.40	2.22×10^{-6}
45	0.77	8.50×10^{-7}	0.31	5.36×10^{-6}
55	0.75	1.93×10^{-7}	0.28	0.06×10^{-6}
		BR buffer pH 11		
25	0.37	5.18×10^{-7}	—	—
35	0.33	1.17×10^{-6}	—	—
45	0.32	1.20×10^{-6}	—	—
55	0.31	1.80×10^{-6}	—	—

TABLE 2 — VALUES OF $k_{f,h}$ AT DIFFERENT TEMPERATURES IN McI AND BR BUFFERS

Temp. °C	$10^4 k_{f,h}$ (I-step) cm sec^{-1}	$10^2 k_{f,h}$ (II-step) cm sec^{-1}	$10^4 k_{f,h}$ (I-step) cm sec^{-1}	$10^3 k_{f,h}$ (II-step) cm sec^{-1}
	pH 3.2 (McI buffer)[a]		*pH 8 (McI buffer)*[b]	
25	9.69	1.08	9.36	—
35	8.36	1.00	6.75	—
45	6.91	0.93	6.44	—
55	6.61	0.89	6.37	—
	pH 2.21 (BR buffer)[c]		*pH 11 (BR buffer)*[d]	
25	8.69	2.93	14.68	—
35	7.70	2.07	12.26	—
45	6.66	1.94	11.71	—
55	6.37	1.86	11.26	—

(a) For step-I, $E_{d.e}$ (vs SCE) = 0.34 V; for step-II $E_{d.e}$ = 0.88 V
(b) For step-I, $E_{d.e}$ = 0.64V;
(c) For step-I, $E_{d.e}$ = 0.24V; for step-II, $E_{d.e}$ = 0.70V
(d) For step-I, $E_{d.e}$ = 0.80V

electrode reaction of nitrobenzene can be studied in terms of values of $k_{f,h}$ at a suitable potential. This potential should be such as to lie in between the potentials corresponding to the foot and the top of the polarographic wave since at such a potential both the rate of electron transfer and the diffusion determine the magnitude of the current[14]. The values of $k_{f,h}$ at a selected potential recorded in Table 2 show that the value of $k_{f,h}$ registers a decrease as the temperature is increased from 25° to 55°C. This decrease in the value of $k_{f,h}$ signifies that the electrode reaction of nitrogbenzene is rendered increasingly more irreversible as the temperature is raised. This

observation is in harmony with the conclusion arrived at on the basis of 'αn_a' values.

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Organotellurium Derivatives : Telluracyclohexane Dihalides, Pseudohalides & Carboxylates

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Several new telluracyclohexane derivatives of the formulae $C_5H_{10}TeX_2$[X=F, CN, NCO, NCS, NCSe, N_3, OCOCH$_3$, OCOH$_2$C$_6$H$_5$, OCOCCl$_3$, OCOC$_6$H$_5$ and OCO(CH$_2$)$_{12}$CH$_3$] have been prepared and characterized on the basis of IR, NMR, conductance and dipole moment data.

IN continuation of our studies on organotellurium halides[1-4] and pseudohalides, we now report the preparation and characterization of several telluracyclohexane dihalides (F,Cl.Br), pseudohalides (CN, NCO, NCS, NCSe, N_3) and carboxylates [OCOR, R = Me, Ph, PhCH$_2$, CCl$_3$, (CH$_2$)$_{12}$CH$_3$], by a metathetical reaction between telluracyclohexane diiodide and the corresponding silver or potassium salts. The dihalides (except the fluoride) have been previously prepared by the direct interaction of tellurium with 1,5-dihalopentane[5] and/or addition of dihalogen to telluracyclohexane[6].

Telluracyclohexane diiodide was prepared by the reported method[6]. Silver salts were freshly prepared before use. Two typical experiments are described below. Other details are given in Table 1. A solu-

TABLE 1 — CHARACTERIZATION DATA OF THE TELLURACYCLOHEXANE DERIVATIVES

Compound	Yield %	m.p. °C	Found (%) (calc)		
			Te	C	H
F	85	210(d)	52.24 (52.85)	25.32 (25.49)	4.22 (4.29)
Cl	80	105 (105)[6]	40.53 (40.76)	—	—
Br	80	106 (107)[6]	35.17 (35.69)	—	—
CN*	65	180(d)	49.77 (50.01)	33.24 (33.70)	4.04 (4.07)
N_3	95	152-53	44.27 (45.81)	21.30 (21.37)	3.24 (3.57)
NCO	85	180(d)	45.12 (45.81)	21.23 (21.3)	3.49 (3.57)
NCS*	45	98–100	40.33 (40.64)	—	—
NCSe	40	120–22(d)	—	—	—
CH$_3$COO	65	52	40.28 (40.34)	34.06 (34.18)	5.48 (5.68)
C$_6$H$_5$COO	74	148–50	28.14 (28.95)	51.24 (51.84)	4.49 (4.58)
C$_6$H$_5$CH$_2$COO	70	133–35	27.00 (27.19)	53.72 (53.75)	5.12 (5.15)
CCl$_3$COO	82	176–78	24.28 (24.32)	35.69 (53.69)	5.13 (5.15)
CH$_3$(CH$_2$)$_{12}$ COO	60	50(d)	19.32 (19.43)	60.26 (60.36)	9.62 (9.82)

*Percentage of CN⁻ or NCS⁻ experimentally found agreed satisfactorily with the calculated values. Further mol. wts of these compounds could not be determined due to insufficient solubility.

tion of telluracyclohexane diiodide (1.0 g, 2.2 mmol) in acetone (40 ml) was stirred with freshly prepared silver thiocyanate (0.5 g, 6 mmol). The precipitated silver iodide was filtered off, the excess solvent distilled under reduced pressure, the separated while crystalline solid washed with pet ether (60–80°) and dried in vaccuo.

A mixture of telluracyclohexane diiodide (1.0 g, 2.2 mmol) and silver oxide (excess) was grinded in minimum quantity of water. To the filtrate was added aqueous hydrofluoric acid in a platinum crucible. Removal of the volatiles under reduced pressure provided the difluoride which recrystallised from acetone.

All the compounds are sharp melting, stable solids excepting the diisocyanate and diisoselenocyanate, which slowly decompose on standing. They are monomeric in freezing benzene and the molar conductances of $10^{-3}M$ solutions in acetonitrile at 30° are in the range 5–30 ohm⁻¹ cm² mol⁻¹, indicating their non-electrolytic character. The dipole moments of the compounds soluble in benzene lie in the range 2.3–3.0 D and may be explained in terms of a distorted trigonal pyramid with the lone pair and organic groups in the equatorial positions as in I

(I)
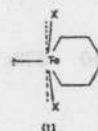
In the IR spectra (ν_{max} in cm⁻¹) of telluracyclohexane derivatives, the νTe-C occurs at 550–520