the present,[13] and more detailed intensity studies of *p*-alkyl substituted derivatives are under way in an effort to clarify the problem.

Summary

Studies of infrared absorption intensity of the C≡N intensity in a series of substituted benzonitrile solutions have permitted the following conclusions: (a) The C≡N intensity is strongly dependent on the properties of the solvent. (b) The relative order of intensities for a series of benzonitriles is essentially unaffected by a change in solvent when the solvent is non-polar or only slightly polar. (c) The intensity for a substituted benzonitrile can be related to a reactivity constant for the substituent. When these constants are compared with rate data taken from the literature it is found that a linear relationship is obeyed in a few cases for electrophilic rate processes.

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URBANA, ILLINOIS

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[13] W. M. Schubert, J. Robins and J. L. Haun, THIS JOURNAL, **79**, 910 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Application of a Theory of Irreversible Polarographic Waves to the Reduction of Nitroalkanes in Non-aqueous Solvents[1]

BY ARTHUR F. FINDEIS, JR., AND THOS. DE VRIES

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A treatment of irreversible polarographic waves controlled by diffusion and rate of reaction is applied to the reduction of nitromethane and 2-methyl-2-nitropropane in methanol, ethanol, isopropyl alcohol and *t*-butyl alcohol. Data are given for αn_α values of the reduction and for the heterogeneous rate constants at zero applied voltage.

A satisfactory theory has been available for the interpretation of polarographic currents controlled by rate of reaction and by diffusion.[2] The application of the appropriate equations to the current-potential curves obtained for the irreversible reduction of organic compounds gives the constant for the rate controlled electrochemical reduction as it depends on the applied potential. It also furnishes the value of the transfer coefficient, α, the fraction of the electrode potential which favors the cathodic reaction process.

In this investigation the reduction of nitro compounds was studied to determine the effect of their structure and the properties of the solvent on the reduction process. Nitromethane and 2-methyl-2-nitropropane were reduced at a dropping mercury electrode in methanol, ethanol and isopropyl alcohol with 0.3 *M* lithium chloride as supporting electrolyte, and in *t*-butyl alcohol with 0.3 *M* lithium perchlorate as the supporting electrolyte. The calculations were based on the use of equations developed by Koutecky[2c] in which he included a term to correct for the movement of the growing mercury drop toward the diffusing species. Heterogeneous rate constants, $k_{f,h}$, were calculated with the equation $\lambda = k_{f,h}t^{1/2}/D^{1/2}$, where λ values are a function of i/i_d, based on maximum currents, D is the diffusion coefficient of the reducible species and t is the drop time.

When the electrode process is the rate-determining step, the relation between the rate constant and the applied potential, E, is $k_{f,h} = k^0_{f,h} \exp(-\alpha\, n_\alpha\, FE/RT)$, where n_α is the number of electrons involved in the rate-determining step and α is the transfer coefficient. Thus log k–E plots give $\alpha\, n_\alpha$ values.

Experimental

All current–voltage curves were obtained using a Leeds and Northrup Electrochemograph, Type E, with no damping of the recorder since maximum currents were desired for the calculations. The validity of the technique was checked by using a more elaborate set up in which a cathode ray oscilloscope was used to determine the true value of the instantaneous current.

The cells were made such that nitrogen could be passed through or over the solution as desired. A presaturator was used in series with the cell when the solutions were degassed with nitrogen passed through a vanadous sulfate solution.[3] All measurements were made at a thermostatically controlled temperature of 25 ± 0.2°.

The capillary had $m^{2/3}t^{1/6}$ values of 2.50 methanol, 2.15 in ethanol, 2.27 in isopropyl alcohol and 2.19 in *t*-butyl alcohol. The corresponding values of t were 2.77, 2.83, 2.51 and 3.14 seconds. These values were determined at voltages corresponding to the beginning of the plateau of the wave. A silver–silver chloride electrode was used as a reference electrode in all solvents except the *t*-butyl alcohol in which lithium chloride was not soluble enough to give a low cell resistance. In this case a mercury pool was used with 0.3 *M* lithium perchlorate as the supporting electrolyte. The cell resistances, measured at the instant of drop fall with a Serfass Conductivity Bridge were as follows: methanol, 500 ohms, ethanol, 950 ohms, isopropyl alcohol, 5,000 ohms and *t*-butyl alcohol, 10,000 ohms.

All of the solvents used were stored over Drierite although it was observed that addition of water up to 1% did not affect the current voltage curves to any measurable extent. Lithium chloride was dried at 110° before use. Lithium perchlorate, anhydrous, was prepared from perchloric acid and lithium carbonate. Ethyl cellulose, viscosity 7.2 seconds, or Triton X-100 (Rohm and Haas Co.) were used as maxima suppressors at a concentration of 0.0025% in the final solution.

After preliminary difficulties it was found that the capillary must be scrupulously clean before each determination to obtain reproducible results. The polarograms obtained with the higher molecular weight alcohols were in general

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[1] Presented at 131st National Meeting of the American Chemical Society, Miami, Florida, April, 1957.

[2] (a) P. Delahay, THIS JOURNAL, **73**, 4944 (1951); **75**, 1430 (1953); (b) P. Delahay and J. E. Strassner, *ibid.*, **73**, 5219 (1951); (c) J. Koutecky, *Collection Czechoslov. Chem. Commun.*, **18**, 597 (1953).

[3] (a) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948); (b) A. F. Findeis, Jr., and Thos. De Vries, *ibid.*, **28**, 209 (1956).

much better but required larger corrections for the *IR* drop through the solution. Because of its insolubility ethyl cellulose could not be used as a maximum suppressor in *t*-butyl alcohol but it was possible to use Triton X-100 in this case.

Results and Discussion

Heterogeneous Rate Constants.—Polarograms were obtained for the reduction of the two nitroalkanes in each of the four solvents. Maximum currents were measured at various potentials along the wave and the average values from six or more independent solutions were used for a composite polarogram. The treatment of Koutecky was applied to this polarographic wave. The parameter $k_{f,h}$ was calculated at various values of E, assuming a constant value of the drop time throughout the reduction step. The diffusion coefficient was calculated from the Ilkovic equation for a maximum current using an electron transfer value of 4. There is general agreement[4] that the reduction of aliphatic nitro compounds proceeds to the corresponding hydroxylamine with the transfer of four electrons and four protons. The data from the polarograms gave excellent straight line log k–E plots which have the slope $\alpha n_{\alpha}/0.0591$.

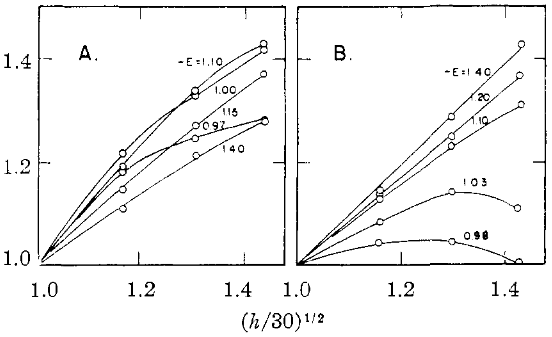

Fig. 1.—Dependence of the diffusion current on the height of the mercury column at various potentials in the reduction of nitromethane in (A) methanol and (B) ethanol.

In Table I are presented data showing the concentrations used, maxima currents observed, the half-wave potentials, the diffusion coefficients and the heterogeneous rate constants at zero applied voltage across the cell. It is not possible to compare values of $k_{f,h}$ at the standard potentials since these are unknown. Excluding the results for the reduction of nitromethane in isopropyl alcohol which appear to be anomalous, the αn_{α} values for 2-methyl-2-nitropropane are slightly smaller than for nitromethane but not enough to be significant. A comparison of the half-wave potentials shows a definite increase to more negative values for 2-methyl-2-nitropropane as the molecular weight of the alcohol increases, the differences being −0.16, −0.18, −0.23 and −0.28, respectively.

Suzuki,[5] with an oscilloscopic technique, has studied the reduction of nitro compounds, including nitromethane, and found that the irreversible reduction to a nitroso compound involving 2 protons and 2 electrons is followed by a reversible reaction involving 2 more protons and 2 electrons at a more positive potential to give an hydroxylamine. Hence we take n_{α} to equal 2 and the transfer coefficient is 0.13 to 0.21 for the compounds studied.

TABLE I

VALUES CALCULATED FROM THE POLAROGRAMS

A. Reduction of nitromethane

Solvent	$M \times 10^4$	i_d, μa.	$-E_{1/2}$	$D \times 10^5$	αn_{α}	$-\log k_{f,h}$ at $E = 0$
CH_3OH	3.84	13.76	1.140	2.56	0.414	10.63
C_2H_5OH	3.76	9.525	1.105	1.74	.330	8.91
$(CH_3)CHOH$	3.80	4.454	0.960	0.334	.494	11.08
$(CH_3)_3COH$	3.91	5.038	1.166	0.431	.331	9.66

B. Reduction of 2-methyl-2-nitropropane

Solvent	$M \times 10^4$	i_d, μa.	$-E_{1/2}$	$D \times 10^5$	αn_{α}	$-\log k_{f,h}$ at $E = 0$
CH_3OH	3.62	12.34	1.302	2.32	0.335	10.03
C_2H_5OH	3.64	9.320	1.294	1.77	.254	8.27
$(CH_3)_2CHOH$	3.64	7.034	1.185	0.91	.259	8.01
$(CH_3)_3COH$	3.62	4.10	1.45	0.334	.327	11.13

Dependence of Current on the Height of the Mercury Column.—Experiments were conducted with the solutions of each of the nitroalkanes in the four alcohols in which the height of the mercury was varied between 30 and 60 cm. at fixed potentials along the polarographic wave. Plots were made of the current ratios, i_h/i_{30}, *vs.* the square root of the mercury height ratios, $(h/30)^{1/2}$, with the h corrected for back pressure. The data obtained for the nitro compounds dissolved in ethanol, isopropyl alcohol and *t*-butyl alcohol agreed with the prediction for a rate controlled reduction.[6] An anomaly was observed for the reduction of both nitro compounds in methanol in that the measured current ratios were larger at positions along the foot of the wave than those observed at the plateau. This is shown in Fig. 1 for nitromethane together with the normal behavior in ethanol.

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LAFAYETTE, INDIANA

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