Bull. Chem. Soc. Jpn., 59, 3815—3820 (1986)

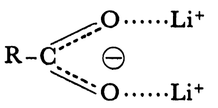
The Specific Effects of Tetraalkylammonium and Alkali Metal Ions on the Polarographic Reduction of Nitroalkanes and Nitrobenzenes in Acetonitrile

Masashi Hojo,* Kazukiyo Nishikawa, Yoshihiro Akita, and Yoshihiko Imai
Department of Chemistry, Faculty of Science, Kochi University, Kochi 780
(Received May 6, 1986)

The polarographic behavior of 2-methyl-2-nitropropane ($(CH_3)_3CNO_2$) was examined at DME in acetonitrile with various supporting electrolytes. The addition of Et_4N^+ or n-Bu_4N^+ caused the half-wave potential ($E_{1/2}$) of $(CH_3)_3CNO_2$ to shift negatively in the presence of a fixed concentration of $NaClO_4$. The negative shift was explained in terms of the interaction between tetraalkylammonium cations and the unreduced molecule of $(CH_3)_3CNO_2$. The formation of $(CH_3)_3CNO_2^{\dot{-}}(Na^+)_2$ was also suggested, and the conditional formation constants of the species were obtained by the positive shift in the $E_{1/2}$ of $(CH_3)_3CNO_2$ with increasing concentration of Na^+ at certain concentrations of Et_4N^+ and n-Bu_4N^+. Other nitroalkanes and nitrobenzenes were also examined. The effect of water on the half-wave potentials of the first waves of the nitro compounds suggested the formation of $RNO_2^{\dot{-}}(H_2O)_2$-type species.

The anion radicals of nitro compounds have attracted a number of electrochemists as well as organic chemists.[1,2] The ion-pair formation between the anion radicals and alkali metal ions in nonaqueous solutions has been suggested both by ESR[3,4] and polarography.[5–7] However, the shift in the half-wave potential of nitrobenzene in polarography has not been connected directly to the thermodynamic value of the ion-pairing.[8] Krygowski et al.[7] tried to evaluate the ion-pair formation constants between the nitrobenzene-anion radical and cations (alkali metal and tetraalkylammonium ions), using the effective ionic potential of the solvated cations in DMF. Kakutani et al.[9] discussed the effect of supporting electrolytes on kinetic paramaters in the polarographic reduction of *p*-nitrotoluene from the point of view of the double-layer theory.

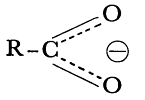
We ourselves have studied polarographically ion-pair formation (or complex formation) reactions between alkali metal ions and carboxylate ions in nonaqueous solvents.[10,11] The formation of the $RCO_2^-(M^+)_2$ (M=Li and Na)-type species was clarified in acetonitrile, one of the protophobic solvents.[11]

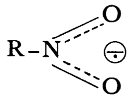


$(R = CH_3, C_6H_5)$

Moreover, we have found that the $RCO_2^-(M^+)_2$ species plays an important role in the polarographic reduction of carboxylic acids in pyridine solutions containing alkali metal ions as the supporting electrolyte cation.[12] Itabashi has proposed the formation of the $[CH_3COOLi_2]^+$ species in the polarographic reduction of copper(II) acetate in acetonitrile containing lithium ions.[13]

Now, let us give our attention to the similarity in the apparent structure between the carboxylate ion (RCO_2^-) and the anion radical ($RNO_2^{\dot{-}}$) of a nitro compound:





In the present investigation, nitroalkanes and nitrobenzenes were examined polarographically in acetonitrile containing tetraalkylammonium (R_4N^+) and alkali metal (M^+) perchlorates as the supporting electrolytes. The specific effects of the coexistence of R_4N^+ and M^+ will be discussed. The effects of proton donors, phenol and water, will also be discussed briefly.

Experimental

Commercial nitro compounds—2-methyl-2-nitropropane ($(CH_3)_3CNO_2$, Aldrich Chemical Company, Inc.), 1-nitrobutane (Aldrich), nitroethane (Wako Pure Chemicals, EP grade), nitromethane (Wako, GR grade), nitrobenzene (Wako, GR grade), and *p*-nitrotoluene (Wako, GR grade)—were used without further purification. Lithium, sodium, tetraethylammonium, and tetrabutylammonium perchlorates were prepared by the methods mentioned previously.[14] The method of purifying acetonitrile has been described elsewhere.[15] Phenol (Wako, GR grade) was used as received.

All the polarograms were recorded with a Yanagimoto polarograph, Model P-1000, and a Watanabe X-Y recorder, Model WX-4401-L0. The rate of the potential sweep was 5 mV s^{-1}. The dropping mercury electrode had the following open-circuit characteristics: m=2.34 mg and τ=2.9 s in a 0.1 M (1 M=1 mol dm^{-3}) Et_4NClO_4-MeCN solution at h=50 cm. The drop time was regulated so as to be 1.0 s by means of a Yanagimoto P-1000-ST drop-timer, except for the potential range of −2.7 V and more negative potentials. The reference electrode was a silver-silver perchlorate electrode, Ag/0.1 M $AgClO_4$-MeCN. All the measurements were carried out at (25±0.2) °C. High-purity nitrogen gas was used for the deoxygenation.

Results and Discussion

Effect of Coexistence of Tetraalkylammonium and Alkali Metal Ions on the Reduction of Nitroalkanes.

Fiure 1 shows polarograms of 2-methyl-2-nitropropane ($(CH_3)_3CNO_2$) in acetonitrile containing various supporting electrolytes. With 0.1 M Et_4NClO_4, 2-methyl-2-nitropropane gave two cathodic waves at −2.07 and −2.85 V. These results are similar to those reported by Sayo et al.[16] with the same supporting electrolyte and solvent. The first wave is attributed to the one-electron reduction of the compound to form the monoanion radical.[16,17] With 0.1 M n-Bu_4N^+ as the supporting electrolyte cation, the second wave was hardly observed. A single wave was given in a 0.1-M $NaClO_4$ solution at a more positive potential than the potential in the tetraalkylammonium perchlorates. The positive shift may suggest interaction between the anion radical and Na^+. The wave height of the cathodic wave of the compound with 0.1 M $LiClO_4$ was larger than that with 0.1 M $NaClO_4$ by the factor of 3, as is shown in Table 1. The large wave height indicates that additional reduction is induced by the presence of Li^+.

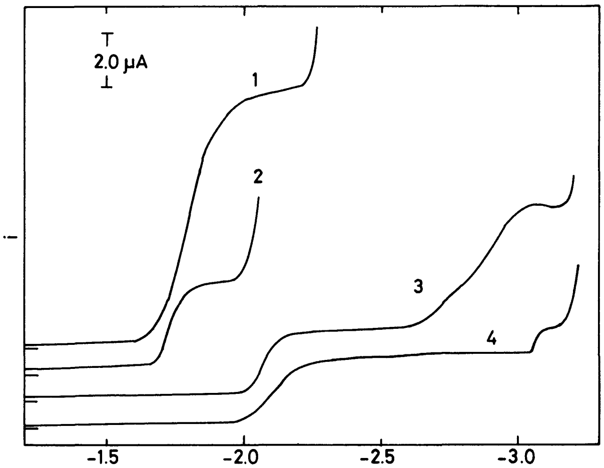


Fig. 1. Polarograms of 2-methyl-2-nitropropane in acetonitrile with various supporting electrolytes. $[(CH_3)_3CNO_2]=0.4$ mM. (1) Li^+, (2) Na^+, (3) Et_4N^+, (4) n-Bu_4N^+ of 0.1 M perchlorate.

Table 1. The Polarographic Data of Nitroalkanes and Nitrobenzenes in Acetonitrile Containing Various Supporting Electrolytes at 25 °C

Supporting electrolyte[a]	First wave $E_{1/2}$[b]/V,	I_l/μA,	Slope[c]/mV	Second wave $E_{1/2}$/V,	I_l/μA,	Slope/mV
	[2-Methyl-2-nitropropane]=0.4 mM					
n-Bu_4N^+	−2.115	2.2	105	—[d]		
Et_4N^+	−2.07	2.2	61	−2.85	4.0	184
Na^+	−1.72	2.8	35			
Li^+	−1.70	8.8	105			
	[1-Nitrobutane]=0.45 mM					
n-Bu_4N^+	−2.00	2.1	63			
Et_4N^+	−1.965	1.9	68			
Na^+	−1.585	2.5	37	−1.94[e]	3.9	97
Li^+	−1.48	7.7	61			
	[Nitroethane]=0.43 mM					
n-Bu_4N^+	−1.97	2.05	68			
Et_4N^+	−1.995	2.35	65			
Na^+	−1.58	2.6	34	−1.96[e]	4.3	93
Li^+	−1.50	8.25	72			
	[Nitromethane]=0.37 mM					
n-Bu_4N^+	−1.955	1.95	79			
Et_4N^+	−1.97	2.15	61			
Na^+	−1.58	3.2	37	−1.99[e]	2.3	79
Li^+	−1.49	6.6	66	(−1.66	2.0	66)[f]
	[Nitrobenzene]=0.35 mM					
n-Bu_4N^+	−1.52	2.1	61	−2.51	5.45	140
Et_4N^+	−1.525	2.1	59	−2.20	5.55	84
Na^+	−1.33[g]	1.85	—	(−1.49	5.0	—)[g]
Li^+	−1.15	3.5	10	−1.30	4.7	85
	[p-Nitrotoluene]=0.41 mM					
n-Bu_4N^+	−1.54	2.05	60	−2.55	4.8	145
Et_4N^+	−1.56	2.1	58	−2.215	5.5	98
Na^+	−1.36[g]	2.05	—	(−1.59	6.5	—)[g]
Li^+	−1.17	3.15	14	−1.32	5.25	84

a) 0.1 M perchlorate. b) vs. Ag/0.1 M $AgClO_4$-MeCN (+0.36 V vs. SCE). c) $-E$ vs. $\log[i/(i_d-i)]$. d) An incomplete wave was given, as is shown in Fig. 1. e) Very close to the reduction potential of the supporting electrolyte cation. f) The other wave appeared just after the first wave. g) Estimated values because of the polarographic maximum.

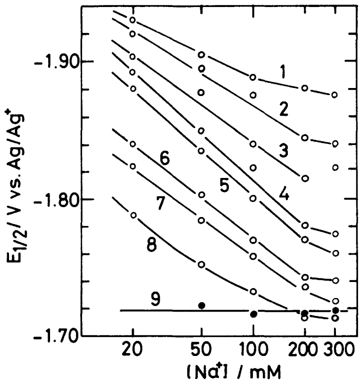


Fig. 2. Effect of Na^+ and n-Bu_4N^+ on the $E_{1/2}$ of 2-methyl-2-nitropropane. $[(CH_3)_3CNO_2]=0.39$ mM. (1) 200, (2) 100, (3) 50, (4) 20, (5) 10, (6) 5, (7) 2, (8) 1, (9) 0 mM of n-Bu_4NClO_4.

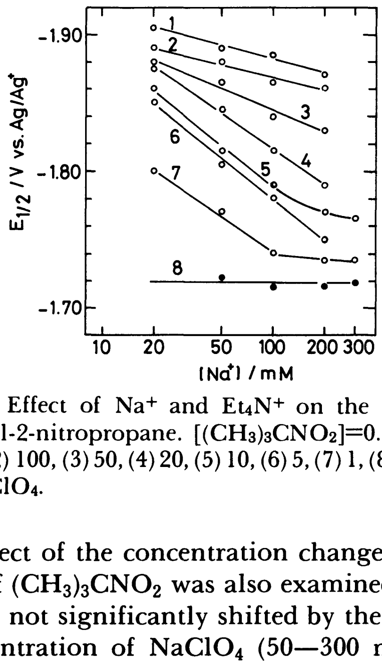


Fig. 3. Effect of Na^+ and Et_4N^+ on the $E_{1/2}$ of 2-methyl-2-nitropropane. $[(CH_3)_3CNO_2]=0.4$ mM. (1) 200, (2) 100, (3) 50, (4) 20, (5) 10, (6) 5, (7) 1, (8) 0 mM of Et_4NClO_4.

The effect of the concentration change of Na^+ on the $E_{1/2}$ of $(CH_3)_3CNO_2$ was also examined. The $E_{1/2}$ value was not significantly shifted by the increase in the concentration of $NaClO_4$ (50—300 mM) in the absence of a tetraalkylammonium salt, as is shown in Fig. 2. However, the addition of a small amount of n-Bu_4NClO_4 caused a remarkable change in $E_{1/2}$. In the presence of 10 or 20 mM n-Bu_4N^+, the $E_{1/2}$ of $(CH_3)_3CNO_2$ was shifted 110 mV to the positive by a 10-fold increase in the concentration of Na^+ ($\Delta E_{1/2}/\Delta\log[Na^+]=110$ mV). The value of $\Delta E_{1/2}/\Delta\log[Na^+]$ decreased to ca. 90 mV with 2 or 50 mM n-Bu_4N^+ and to smaller values with 1 or 100 mM n-Bu_4N^+. The waves were diffusion-controlled in the presence of both 10—100 mM n-Bu_4N^+ and 20—100 mM Na^+. The slope of $-E$ vs. $\log[i/(i_l-i)]$ was ca. 60 mV for 20—100 mM $NaClO_4$ with 5—20 mM n-Bu_4NClO_4 and for 200 mM $NaClO_4$ with more than 50 mM n-Bu_4NClO_4. The polarographic behavior with Et_4N^+ and Na^+ was quite similar to that with n-Bu_4N^+ and Na^+, except that the slope of $\Delta E_{1/2}/\Delta\log[Na^+]$ was, at most, 100 mV at 5 and 10 mM of Et_4N^+ (cf. Figs. 2 and 3).

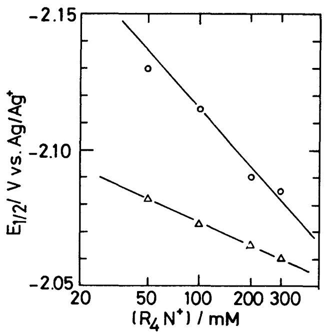


Fig. 4. Effect of the concentration of the supporting electrolyte on the $E_{1/2}$ of the first wave of 2-methyl-2-nitropropane. $[(CH_3)_3CNO_2]=0.4$ mM. (○): n-Bu_4NClO_4, (△): Et_4NClO_4.

The data given in Figs. 2 and 3 may be analyzed by means of the following equations, in which ion-pair formation and "complex-formation" reactions are taken into account:

$$(\Delta E_{1/2})_{\mathrm{R_4N^+}} = \frac{0.059}{n}\log K' + \frac{0.059}{n}p\log[\mathrm{M^+}] \qquad (1)$$

$$(\Delta E_{1/2})_{\mathrm{M^+}} = -\frac{0.059}{n}\log K'' - \frac{0.059}{n}q\log[\mathrm{R_4N^+}] \qquad (2)$$

where $(\Delta E_{1/2})_{\mathrm{R_4N^+}}$ means the change in $E_{1/2}$ caused by the addition of M^+ at a constant concentration of R_4N^+ and where $(\Delta E_{1/2})_{\mathrm{M^+}}$ is that caused by the addition of R_4N^+ at a constant concentration of M^+. K' and K'' are the conditional formation constants. p and q are the numbers of M^+ and R_4N^+ "coordinated" to the anion radical and the unreduced nitro compound respectively. The other conditions for Eqs. 1 and 2 are similar to those given in Ref. 11. For a fixed concentration of n-Bu_4N^+ (e.g., 10 mM), the value of p is derived as 2 from the slope of 110 mV and $n=1$. On the other hand, q equals ca. 1 at a constant concentration of Na^+ (e.g., 50 mM), as will be described in detail below. The fact that $p=2$ and $q=$ca. 1 for $(CH_3)_3CNO_2$ can be explained by the following scheme:

$$\begin{tikzcd}
\mathrm{(CH_3)_3CNO_2} \arrow[r, shift left, "e^-"] \arrow[d, shift left, "n\text{-}\mathrm{Bu_4N^+}"' , "K''"] & \mathrm{(CH_3)_3CNO_2^{\cdot-}} \arrow[l, shift left] \arrow[d, shift left, "\mathrm{2Na^+}", "K'"'] \\
\mathrm{(CH_3)_3CNO_2\cdot}n\text{-}\mathrm{Bu_4N^+} \arrow[u, shift left] & \mathrm{(CH_3)_3CNO_2^{\cdot-}(Na^+)_2} \arrow[u, shift left]
\end{tikzcd}$$

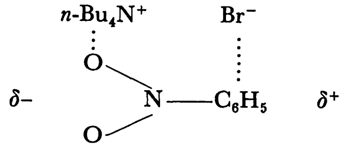
The conditional formation constant of the sodium complex was given as $\log(K'/M^2)=9._6$ in the presence of 10 mM n-Bu_4N^+. The $E_{1/2}$ value for the case of $[n\text{-}Bu_4N^+]=10$ mM without Na^+ was estimated by the extrapolation from the $E_{1/2}$ values with 50—300 mM n-Bu_4N^+ (see Fig. 4). The irreversibility of the wave with n-Bu_4N^+ alone was ignored in this case. Similarly, $\log(K'/M^2)$ of $7._7$ was obtained for $[Et_4N^+]=10$ mM from Fig. 3.

The degree of interaction between n-Bu_4N^+ and $(CH_3)_3CNO_2$ is expressed by the other conditional formation constant, K''. For a constant concentartion of Na^+ (50 mM), the $E_{1/2}$ shifted ca. 65 mV negatively upon a 10-fold increase in the concentration of n-Bu_4N^+ (from 2 to 20 mM). In the presence of 50 mM Na^+, log (K''/M^2) was estimated to be ca. $4._4$ for n-Bu_4N^+. Log (K''/M^2) was $3._8$ for the interaction between Et_4N^+ and $(CH_3)_3CNO_2$ in the presence of 50 mM Na^+.

Strange to say, the half-wave potential of the first wave of $(CH_3)_3CNO_2$ shifted positively with increasing concentration of n-Bu_4N^+ or Et_4N^+ ($\Delta E_{1/2}/\Delta \log[R_4N^+]=$ ca. 70 and 30 mV for n-Bu_4N^+ and Et_4N^+ respectively) without Na^+, as is shown in Fig. 4. The positive shift suggested the interaction between the R_4N^+ ion and the anion radical. The interaction between the tetraalkylammonium cations and the anion radical of nitrobenzene[7] has also been suggested by the positive shift in the $E_{1/2}$ of the reduction wave of nitrobenzene in DMF solutions. As has been shown above, the half-wave potential shifted negatively with increasing concentration of R_4N^+ in the presence of Na^+. The shifts of opposite directions between the absence and presence of Na^+ can be cleared up by the following idea: The $RNO_2^{\cdot-}$ ion as well as RNO_2 interacts with R_4N^+ in the absence of Na^+. However, the strong interaction of Na^+ with $RNO_2^{\cdot-}$ (the formation of $RNO_2^{\cdot-}(Na^+)_2$) prevents the R_4N^+ ion from interacting with $RNO_2^{\cdot-}$.

The strength of these interactions may vary with the concentration ratio between R_4N^+ and Na^+. We think that two interactions in opposite directions bring the change in the slope in Figs. 2 and 3. The minor change in the half-wave potentials with the concentration change of Na^+ in the absence of R_4N^+ can not be explained exactly at the present time, although the positive potential shift (+0.35 V) by 0.1 M $NaClO_4$, compared with 0.1 M Et_4NClO_4 (see Table 1), suggested interaction between the anion radical and Na^+. The slope of $\log[i/(i_d-i)]$ with 0.1 M $NaClO_4$ alone was rather small (35 mV). The reduction process of 2-methyl-2-nitropropane in acetonitrile seems not to be straightforward with alkali metal cations in the absence of tetraalkylammonium cations. At any rate, we have given a quantitative explanation for some typical cases in the extraordinary phenomena, without considering the other reactions or the double-layer effect.

Hyne has reported interaction between the neutral molecule of nitrobenzene and tetrabutylammonium bromide in a mixture of nitrobenzene and methanol, based on the conductivity data etc.[18] His proposal seems to support our mechanism, in which the interaction between the nitro compound and R_4N^+ is accounted.



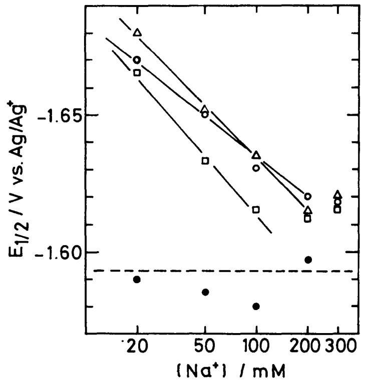


Fig. 5. Change of $E_{1/2}$ of nitroalkanes with Na^+ concentration. (○): 1-Nitrobutane, (△): nitroethane, (□): nitromethane in the presence of 10 mM n-Bu_4NClO_4, (●): 1-nitrobutane, in the absence of n-Bu_4NClO_4. The concn. of a nitroalkane is 0.4 mM.

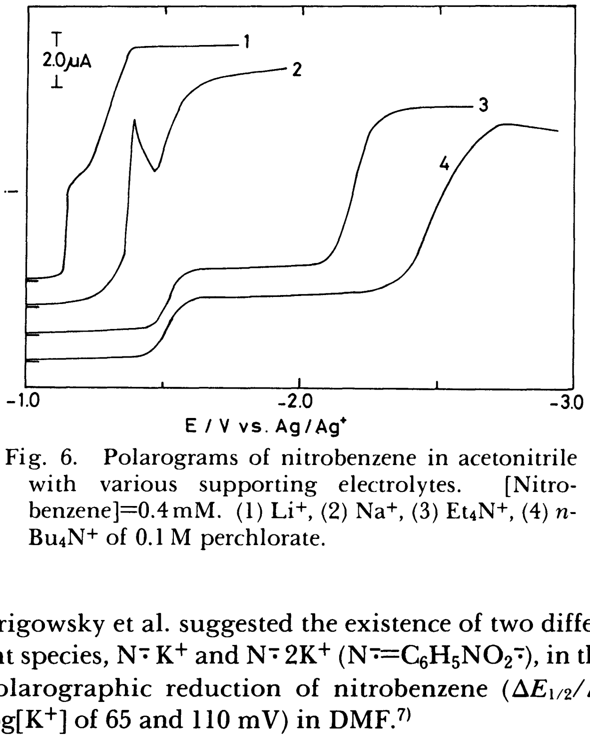


Fig. 6. Polarograms of nitrobenzene in acetonitrile with various supporting electrolytes. [Nitrobenzene]=0.4 mM. (1) Li^+, (2) Na^+, (3) Et_4N^+, (4) n-Bu_4N^+ of 0.1 M perchlorate.

Krigowsky et al. suggested the existence of two different species, $N^{\cdot-}K^+$ and $N^{\cdot-}2K^+$ ($N^{\cdot-}=C_6H_5NO_2^{\cdot-}$), in the polarographic reduction of nitrobenzene ($\Delta E_{1/2}/\Delta \log[K^+]$ of 65 and 110 mV) in DMF.[7]

As for other nitroalkanes, the values of the $\Delta E_{1/2}/\Delta \log[Na^+]$ slope were 50, 65, and 80 mV for 1-nitrobutane, nitroethane, and nitromethane respectively in the presence of 10 mM n-Bu_4N^+, as is shown in Fig. 5. These values suggest the interaction of the anion radical with a single Na^+ ion ($RNO_2^{\cdot-}Na^+$) or more in the presence of 10 mM n-Bu_4N^+. The half-wave potential of 1-nitrobutane was not so much influenced by the concentration change of $NaClO_4$ in the absence of n-Bu_4NClO_4. The increase in the concentration of n-Bu_4NClO_4 caused the half-wave potential of the first wave of 1-nitrobutane to shift positively (e.g., $E_{1/2}=-2.02$ V at 20 mM and -1.99 V at 200 mM of n-Bu_4N^+) without $NaClO_4$.

On the Reduction of Nitrobenzenes. Polarographic data of nitrobenzene and p-nitrotoluene with var-

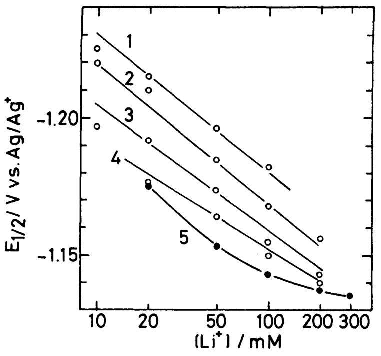


Fig. 7. Effect of Li^+ and Et_4N^+ on the $E_{1/2}$ of the first wave of nitrobenzene. [Nitrobenzene]=0.39 mM. (1) 100, (2) 50, (3) 20, (4) 5, (5) 0 mM of Et_4NClO_4.

ious supporting electrolytes are also listed in Table 1. Nitrobenzene gave two cathodic waves with each supporting electrolyte (Fig. 6). The first wave showed a good reversibility with 0.1 M n-Bu_4N^+ or Et_4N^+. However, the slope of $-E$ vs. $\log[i/(i_d-i)]$ was extremely small (10 mV) with 0.1 M Li^+. The small slope observed with Li^+ became larger (≈30 mV) upon the addition of 0.1 M n-Bu_4N^+ or Et_4N^+. The half-wave potential of nitrobenzene shifted positively ca. 50 mV ($\Delta E_{1/2}/\Delta\log[Li^+]$) with increasing concentration of $LiClO_4$ in the presence of 20—100 mM Et_4N^+, as is shown in Fig. 7. With 50 mM Et_4N^+, the highest slope (52 mV) was obtained. For p-nitrotoluene, the slope was 58 mV with a concentration change of Li^+ at 50 mM n-Bu_4N^+. From the data in Fig. 7, $p=1$ and $q=$ca. 0.5 in Eqs. 1 and 2 were derived for nitrobenzene, assuming $n=1$. The fact that $p=1$ in the presence of both Li^+ and Et_4N^+ suggests the following reaction:

$$\mathrm{C_6H_5NO_2^{\overline{\cdot}}} + \mathrm{Li^+} \overset{K'}{\rightleftarrows} \mathrm{C_6H_5NO_2^{\overline{\cdot}}Li^+} \qquad (3)$$

The interaction between the nitrobenzene molecule and the Et_4N^+ cation was also suggested, even though the value of q was not unity.

The difference in the number of alkali metal ions "coordinated" to the anion radicals between 2-methyl-2-nitropropane ($p=2$) and nitrobenzene ($p=1$) seems to be caused by the difference in the electron density on the nitro group. Peover and Powell described[19] that, in the anion radical of an aliphatic compound, the charge on the nitro group is virtually unity, while in that of a nitrobenzene, the charge can be delocalized into the aromatic system.

Effect of Proton Donors on the Reduction Wave of Nitro Compounds. The effect of phenol on the polarographic reduction of 2-methyl-2-nitropropane was examined. By the addition of 10 mM of phenol to a 0.4 mM $(CH_3)_3CNO_2$ solution, the two waves of $(CH_3)_3CNO_2$ without phenol merged into a single wave of $E_{1/2}=-1.97$ V. The wave height with 10 mM phenol was 3—4 times as large as the first wave height without phenol. The further addition of phenol up to 100 mM caused the half-wave potential to shift positively, without changing the wave height.

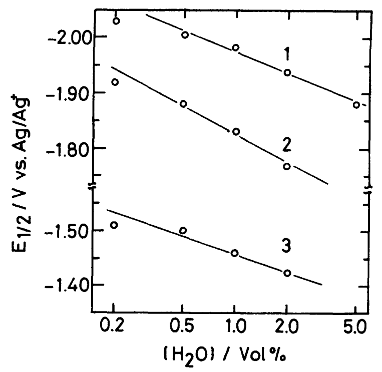
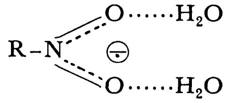


Fig. 8. Effect of H_2O on the $E_{1/2}$ of the first wave of nitroalkanes and nitrobenzene in acetonitrile solutions containing 0.1 M Et_4NClO_4. (1) 2-Methyl-2-nitropropane, (2) nitromethane, (3) nitrobenzene. The concns. of the nitro compounds are all 0.4 mM.

Figure 8 shows the effect of H_2O on the half-wave potentials of 2-methyl-2-nitropropane, nitromethane, and nitrobenzene. The half-wave potentials of $(CH_3)_3CNO_2$ and nitrobenzene both shifted ca. 120 mV positively upon a 10-fold increase in the water concentration. The wave height of $(CH_3)_3CNO_2$ or nitrobenzene (the first wave) remained constant even upon the addition of water up to 2% (2.15 μA, cf. 2.1 μA without water for $(CH_3)_3CNO_2$). The waves were reversible and seemed to be diffusion controlled. Therefore, the value of 120 mV for $\Delta E_{1/2}/\Delta\log[H_2O]$ suggested that the anion radicals of $(CH_3)_3CNO_2$ and nitrobenzene interact with two molecule of water:



We have previously reported elsewhere[11] the interaction between the benzoate ion ($C_6H_5CO_2^-$) and two molecules of water in an acetonitrile solution.

For nitromethane, the value of $\Delta E_{1/2}/\Delta\log[H_2O]$ was 145 mV, which may also suggest the interaction between the anion radical of nitromethane and two molecules of water.

Lipsztajn et al.[20] have reported the experimental results that the slope of $\Delta E_{1/2}/\Delta\log[H_2O]$ is ca. 120 mV (0.1—1 M H_2O) for the half-wave potential of the first wave of nitrobenzene in DMF containing 0.1 M Et_4NClO_4 as the supporting elctrolyte. They[20] suggested the formation of both $NB^{\overline{\cdot}}\,Na^+$ and $NB^{\overline{\cdot}}\,2Na^+$ ($NB^{\overline{\cdot}}$ =nitrobenzene anion radical) in DMF containing 1.66 M of H_2O (3% by volume).

We wish to express our thanks to Professor Toyokichi Kitagawa of Osaka City University for his helpful suggestions.

References

1) C. K. Mann and K. K. Barnes, "Electrochemical Reac-

tions in Nonaqueous Systems," Marcel Dekker, New York (1970), p. 347.

2) O. Popovych and R. P. T. Tomkins, "Nonaqueous Solution Chemistry," John Wiley and Sons, New York (1981), p. 362.

3) T. Kitagawa, T. Layloff, and R. N. Adams, *Anal. Chem.*, **36**, 925 (1964).

4) J. Oakes, J. Slater, and M. C. R. Symons, *Trans. Faraday Soc.*, **68**, 546 (1970).

5) L. Holleck and D. Becher, *J. Electroanal. Chem.*, **4**, 321 (1962).

6) L. A. Avaca and A. Bewick, *J. Electroanal. Chem. Interfacial Electrochem.*, **41**, 405 (1973).

7) T. M. Krygowski, M. Lipsztajn, and Z. Galus, *J. Electroanal. Chem. Interfacial Electrochem.*, **42**, 261 (1973).

8) T. Osa, "Denkyoku-hannō No Kiso," ed by T. Osa, Kyōritsu Shuppan, Tokyo (1973), p. 205.

9) T. Kakutani, H. Kinoshita, and M. Senda, *Review of Polarography* (*Japan*), **20**, 15 (1974).

10) M. Hojo and Y. Imai, *Bunseki Kagaku*, **32**, E77 (1983).

11) M. Hojo and Y. Imai, *Bull. Chem. Soc. Jpn.*, **56**, 1963 (1983).

12) M. Hojo, Y. Akita, K. Nishikawa, and Y. Imai, *Bull. Chem. Soc. Jpn.*, in press.

13) E. Itabashi, *J. Electroanal. Chem. Interfacial Electrochem.*, **36**, 179 (1972).

14) T. Fujinaga, S. Okazaki, and M. Hojo, *Bull. Inst. Chem. Res., Kyoto Univ.*, **56**, 139 (1978).

15) T. Fujinaga, S. Okazaki, and M. Hojo, *J. Electroanal. Chem. Interfacial Electrochem.*, **113**, 89 (1980).

16) H. Sayo, Y. Tsukitani, and M. Masui, *Tetrahedron*, **24**, 1717 (1968).

17) A. K. Hoffmann, W. G. Hodgson, and W. H. Jura, *J. Am. Chem. Soc.*, **83**, 4675 (1961).

18) J. B. Hyne, *J. Am. Chem. Soc.*, **85**, 304 (1963).

19) M. E. Peover and J. S. Powell, *J. Electroanal. Chem. Interfacial Electrochem.*, **20**, 427 (1969).

20) M. Lipsztajn, T. M. Krygowski, and Z. Galus, *J. Electroanal. Chem. Interfacial Electrochem.*, **49**, 17 (1974).