The Solvent Effect on the Catalytic Activity of Benzonitrile-Alkali Ion Salt Solutions for the Hydrogen Exchange Reactions

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Recently it has been reported that the activation of hydrogen takes place by means of some electron donor-acceptor (EDA) complexes of aromatic compounds with alkali metals in their solutions as well as in the solid state.1) It was previously shown that the hydrogen absorption and the hydrogen exchange reaction proceeded homogeneously at room temperature in the anthracene dianion complex solutions,2) much as on their films.3) We would like to report here a marked solvent effect on the catalytic activity by the benzonitrile-alkali ion radical salt solutions for the hydrogen exchange reactions, especially, there is a strong inhibition of alkali cations by chelating solvents.

Benzonitrile-alkali ion radical salts were prepared in solution by a reaction between benzonitrile (10^{-4}—10^{-2} mol) and each of the alkali metals in *ca.* 80 cc of dry THF (tetrahydrofuran), MDE (monoethylene glycol dimethyl ether), DED (diethylene glycol dimethyl ether), TED (triethylene glycol dimethyl ether) and benzonitrile, much as has been described previously.4) The composition of the complexes was confirmed by a study of their electronic spectra. Each of the complex solutions was introduced into a reaction vessel (*ca.* 270 cc) through a glass filter in order to remove an excess of the unreacted metal. When D_2 (10—45 cm Hg) was introduced to the complex solution, which was strongly stirred, the gaseous deuterium was reversibly exchanged with the hydrogen of the complex molecule in the temperature range from -20 and 50°C; a small amount of hydrogen was absorbed5) at the same time in the benzonitrile-sodium or -lithium solution. The initial rates (in the first-order kinetics) or HD formation in the D_2–HZ ($HZ=PhCN^-M^+$; M=Li, Na, K, and Rb) exchange reaction are given in Table 1. It was demonstrated by the NMR spectrometry6) that the $PhCN^-K^+$ complex was deutrated at the *p*-position of benzonitrile. The kinetics of the D_2–HZ exchange reaction was also investigated by changing the D_2 pressure and the concentration of the $PhCN^-K^+$ in THF (1.2×10^{-2}—2.8×10^{-3} mol):

$$V_{HD}=kP_{D_2}(PhCN^-K^+)^2$$

Table. 1

Complex(HZ) (1.2×10^{-3} mol)	Solvent (80 cc)	D_2–HZ exchange reaction	
		K_{HD}(cc/hr)	E(kcal/mol)
$PhCN^-Li^+$	THF	0.1	16
$PhCN^-Na^+$	THF	4.8	10
$PhCN^-K^+$	THF	10.0a)	6
$PhCN^-Rb^+$	THF	0.3	—
$PhCN^-K^+$	MED	2.0	—
$PhCN^-K^+$	DED	0.58	—
$PhCN^-K^+$	TED	0.32	—
$PhCN^-K^+$	PhCN	>0.001	—
$PhCN^-K^+$	THF	>0.2	—
	(9×10^{-3} mol; PhCN)		

a) The HD formation in the D_2–HZ exchange reaction took place homogeneously to reach nearly a monodeuteration of $PhCN^-K^+$ complex:

$$\frac{N_{exch.}}{(PhCN^-K^+)}=0.87\ (25°C)$$

Where $N_{exch.}$ denotes the total number of the hydrogen exchanged with deuterium gas.

It was interesting to note in Table 1 that the activity of the $PhCN^-M^+$ solution decreased strikingly when strong chelating solvents were used with alkali cations, such as DED, TED, or benzonitrile. When a small amount of benzonitrile (0.9×10^{-2} mol) was added to the THF solution of the benzonitrile – K stoichiometric complex, the exchange rates decreased; they were retarded completely by the addition of an excess.

The D_2–HZ and H_2–D_2 exchange reactions exhibited wide varieties of activities in solution; this was in contrast to the reactions over their complex films under similar reaction conditions.7) The characteristic behaviour of such chelating solvents might be attributed to the solvation to alkali cations, which brings about a wide separation between anion and cation centers8) in the complex molecule, thus preventing the development of favorable circumstances for the hydrogen activation.

A similar behavior of the different solvents was observed for the hydrogen exchange reaction and hydrogen absorption in their complex solutions, such as anthracene dianion, naphthalene monoanion and cyanonaphthalene dianion with alkali cations.

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1) M. Ichikawa, M. Soma, T. Onishi, and K. Tamaru, This Bulletin, **43**, 3672 (1970), references therein.

2) M. Ichikawa and K. Tamaru, *J. Amer. Chem. Soc.*, in press.

3) M. Ichikawa, S. Tanaka, S. Naito, M. Soma, T. Onishi, and K. Tamaru, *Trans. Faraday Soc.*, submitted for publication.

4) M. Ichikawa, S. Tanaka, S. Naito, M. Soma, T. Onishi, and K. Tamaru, *Trans. Faraday Soc.*, **66**, 981 (1970).

5) It was shown by the NMR and UV spectrometry that the $PhCN^-Na^+$ and $PhCN^-Li^+$ were decomposed very slowly at room temperature in the presence of hydrogen gas to produce benzonitrile and metal hydride (NaH and LiH).

6) After deuteration and the removal of the solvent, the $PhCN^-K^+$ complex was oxidized to neutral PhCN by dry oxygen gas at 25°C as measured by mass and NMR spectrometry.

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8) M. Szwarc, *Prog. Phys. Org. Chem.*, **6**, 323 (1969); T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307, 318 (1966).