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# THE ABILITY OF CROWN ETHERS TO INCREASE THE SPECIFIC ACTIVITY OF POTASSIUM ALKOXIDES IN DMSO

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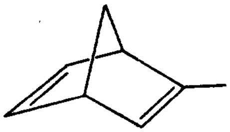
The use of crown ethers(1) as strong complexing agents for metal cations, especially those of the alkali metals, has been well documented over the past several years.(2) In most of the cases studied it has been assumed or shown that the metal cation is encompassed by a ring or donut of ether oxygens.(2b) In one of our examinations of this complexing behavior we have now shown that specifically 18-crown-6(III)(3) has the ability to satisfy completely the coordination sites of a potassium ion even to the exclusion of strongly solvating molecules such as DMSO.

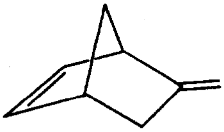
The rates of carbanion generation via proton abstraction from hydrocarbon substrates have been used as a probe for determining the states of aggregation and hence the related base strength of strong bases in a variety of solvents.(4) Specifically, the potassium *tert*-butoxide catalyzed formation of carbanions has been found to be dependent on both the specific solvent system and the concentration of base. In *tert*-butanol the pseudo first order rates of proton abstraction show only slight dependence on *tert*-butoxide at low concentrations and 0 order dependence at high concentrations. In DMSO this profile changes slightly so that at low concentrations the rates approach 1st order in base while at higher concentrations they also approach an 0 order. This rate behavior has been explained by invoking a series of mobile equilibria between aggregates of *t*-BuOK, monomeric *t*-BuOK, and the solvent.

$$n\ \textit{t}\text{-BuOK} \rightleftarrows (\textit{t}\text{-BuOK})_2 \rightleftarrows \ldots \rightleftarrows (\textit{t}\text{-BuOK})_n$$

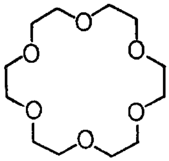
Since DMSO is a good solvent for ions, readily forming solvent separated ion pairs, it shifts each of these equilibria toward the more ionic,



I



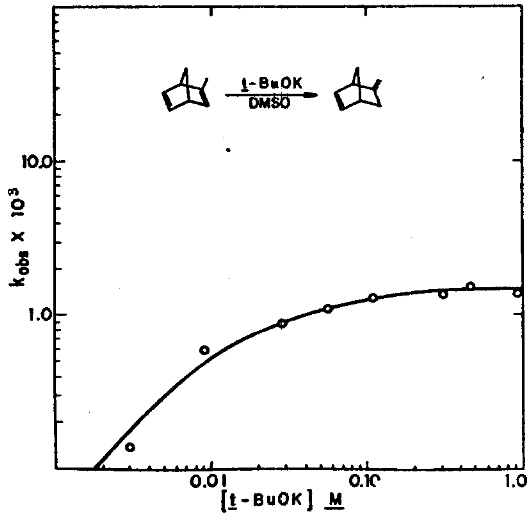
II

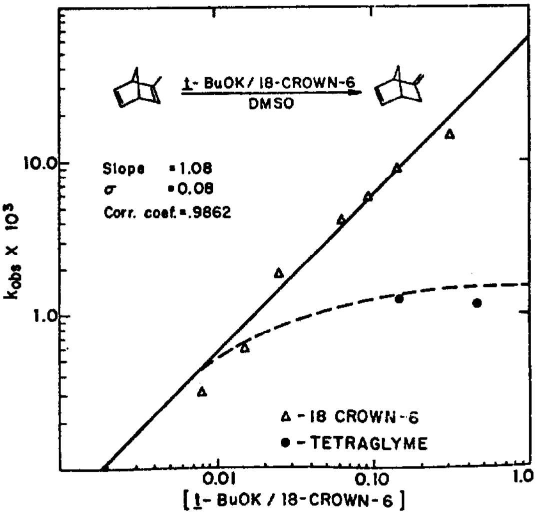


III

monomeric base species. At high concentrations of base, though, aggregation becomes important to the point that each added molecule of base merely adds to the total of aggregated species. Tert-butanol, being a poor solvent in itself, is unable to support solvation of ion paris and the resulting activity of the solution is that of a small concentration of monomeric base in equilbrium with a large concentration of aggregated species.

The present study has measured the rate behavior as a function of base concentration for the isomerization of 2-methylbicyclo(2.2.1)hepta-2,5-diene (I) to 5-methylenebicyclo(2.2.1)hept-2-ene (II) by t-BuOK in DMSO. Through equilibration studies we predetermined that the equilibrium for this reaction lies >99% toward II. The starting hydrocarbon I was prepared by





reacting bicyclo(2.2.1)hepta-2,5-diene in ether with butyllithium, followed by quenching at -50°C with methyl iodide. Distillation (122-123°) of the crude product gave essentially a pure mixture of I and II (glpc analysis give 94% (I), 5% (II), ~1% others). Tert-BuOK, MSA reagent grade, was sublimed three times and stored in a dry box prior to use; DMSO was purified, after freeze degassing, by vacuum distillation at <50°C from sodium amide and was analyzed at <1 ppm $H_2O$ (Karl Fischer).(5) Sublimed 18-crown-6 (III) was used.(6) All solutions and transfers were done in a dry box or with gas tight syringes. For the kinetics, a stock solution of t-BuOK in DMSO (0.33 M) was distilled with fresh DMSO and added to a serum capped vial, the vial was then equilibrated for 30 minutes in a 50° bath. To initiate the reaction, 40 μℓ of I (making ~0.03M) was injected through the serum cap. Points were taken by removing, under $N_2$, aliquats and quenching in ice/water/hexane. The hexane was washed several times, dried, and injected into the glpc to follow isomerization. All kinetics were followed to >95% completion; all gave good linear first order plots.

The two accompanying graphs show the dependence of the pseudo first order rate constants for isomerization on the concentration of t-BuOK. Since $k_1^{obs}$, the pseudo first order rate constant, equals $[\text{Base}]^{\alpha}k_2$, the slope of a log-log plot of $k_1^{obs}$ vs. [Base] will give directly the kinetic order in base. For the system studied in DMSO, the behavior is that described earlier. At base levels >0.1 M there is 0 order base dependence, while at lower concentrations the order is variable, approaching 1st order at higher dilutions.

Compare this with the effect of running the same kinetics with a molar equivalent of 18-crown-6 ether to complex the potassium ion. Within the limits of experimental error, the kinetics follow 1st order base dependency between the range 0.01 M to 0.33 M. This represents a significant increase in the concentration of non-aggregated base (at least a power of ten) compared to the same reaction in pure MDSO. As a comparison with other non-cyclic polyethers, two points are shown for molar equivalents of tetraglyme. These may be taken to be identical with the DMSO line, the small rate decrease is probably due to a change in the overall dielectric constant caused by the introduction of 0.3 M of low dielectric ether. The comparison shows that this rate behavior is specific for the cyclic polyether structure not merely polyether complexation.

Examination of these curves can bring out several important facts. At low concentrations of base the lines for both complexed and uncomplexed t-BuOK in DMSO are superimposable. This implies that in both cases the base is mostly monomeric and probably solvent separated. At these concentrations a change in the solvent shell from DMSO to 18-crown-6 does not affect either the degree of aggregation or the ion-pair character of the base and this is reflected in the similarity of the absolute rates and kinetic order in base. At higher concentrations of t-BuOK, pure DMSO is not capable of maintaining complete solvent separation of the t-BuO-$K^+$ ions and ionic aggregation begins to appear. At this point we see the strong attraction of 18-crown-6 for $K^+$. Even when DMSO is incapable of satisfying the solvation demands for $K^+$, it appears that a $K^+$ -18-crown-6 complex is completely free of further solvation demands.

These results point out the ability to improve dramatically the activity of $K^+$ salts, even in highly solvating media, by the addition of an equivalent of 18-crown-6 cyclic polyether.

## REFERENCES

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5. All analyses were performed by the Elastomer Chemicals Department analytical division.
6. Kindly supplied by R. N. Greene.