

in Figure 1 for the dimensional changes that result from such libration.

**Disorder in the Room-Temperature Solid.** The diffuse X-ray scattering at room temperature provides additional information on the thermal vibrations of both crystallographically independent molecules and on the disorder associated with molecule II. Precession photography reveals prominent diffuse scattering normal to (010) and to the scattering vectors through the reciprocal lattice points  $201$ ,  $10\bar{2}$ ,  $10\bar{4}$  and  $20\bar{4}$ . The scattering extends on precession photographs at least through  $241$ ,  $13\bar{2}$ ,  $12\bar{4}$  and  $22\bar{4}$ , respectively: it may be noted that the long  $b$  axis results in a close spacing of reciprocal layers normal to  $[010]$ . The interplanar spacing between molecules in direct space is  $\sim 3.6$  Å. The minimum vector between planes of molecule I corresponds in reciprocal space to the location  $0.8, 0.1, -2.0$ , which is close to  $10\bar{2}$ . The second order of this vector is also clearly visible on precession photographs around  $10\bar{4}$  and  $20\bar{4}$ . The corresponding vector between planes of molecules II terminates at  $1.9, 2.4, 0.9$ , which is close to  $221$  and  $231$ . The molecular librations of pairs of symmetry related molecules hence give rise to the diffuse scattering centered at these strong reflections.

Additional continuous diffuse bands of X-ray scattering appear between  $\bar{2}00$  and the forbidden  $001$ , between  $001$  and  $202$ , and between  $\bar{2}01$  and  $002$ . The direction normal to these bands corresponds to the orientation of planes composed of molecules II, which form layers throughout the crystal (see Figure 2). The spacing of these diffuse bands is consistent with the intermolecular center-to-center distance of  $9.2$  Å. The diffuse bands may be interpreted as arising from short range order caused by the correlated orientations of molecules II. Such correlation is necessary to avoid the formation of short intermolecular O...O contacts.

**Heat Capacity.** The likelihood that the disorder associated with molecule II is temperature dependent, and the possibility of a phase transition occurring if ordering took place, led to a preliminary study of the heat capacity.<sup>23</sup> A first-order phase transition was detected at  $252$  K; a second transition starts at  $330$  K and is not complete until  $395$  K, on heating. Both transitions are reversible and reproducible. Further investigation of these transitions has been undertaken.

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**Supplementary Material Available:** A listing of the measured and calculated structure factors for 9-hydroxyphenalenone (Table IV) (12 pages). Ordering information is given on any current masthead page.

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## Decarboxylation of 6-Nitrobenzisoxazole-3-carboxylate in Benzene Catalyzed by Crown Ethers and Their Polymers

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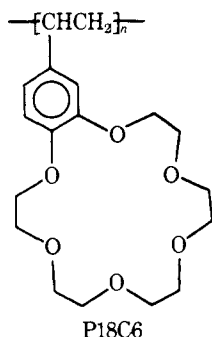
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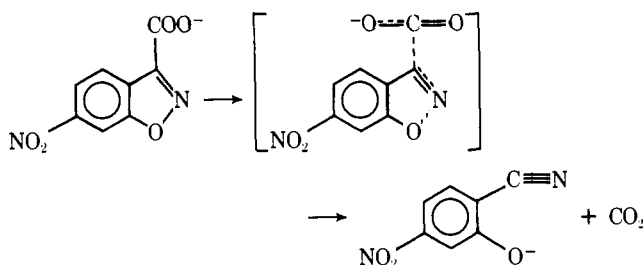
**Abstract:** Rate constants and activation parameters of decarboxylation of potassium 6-nitrobenzisoxazole-3-carboxylate (I) were measured in benzene in the presence of 4'-methylbenzo-18-crown-6, 18-crown-6, cryptand 2.2.2, and the homopolymer (P18C6) and styrene copolymers of 4'-vinylbenzo-18-crown-6. The crown-complexed ion pairs of I decompose with rate constants in the order of  $0.1$ – $1.0$  s<sup>-1</sup> at  $25$  °C, depending on the crown compound. The rate constant for the cryptated ion pair ( $4.78$  s<sup>-1</sup> at  $25$  °C) is nearly identical with that found for the decarboxylation of I in dimethyl sulfoxide and more than a thousand times higher than previously found for the tetramethylguanidinium salt of I in benzene. The crown ethers are believed to be externally complexed to the tight potassium carboxylate ion pair. For polymers with a high content of crown ligands, the rate constant of decarboxylation increases, probably as a result of an enlargement in the interionic distance of the crown complexed ion pair.

We recently reported<sup>1,2</sup> that poly(4'-vinylbenzo-18-crown-6), abbreviated in this paper as P18C6, catalyzes the

decomposition of 6-nitrobenzisoxazole-3-carboxylate (I) in water. The decarboxylation, a unimolecular, concerted, in-



intermediateless E<sub>2</sub> elimination reaction,<sup>3-5</sup> is slow in water ( $k_{25^\circ\text{C}} = 3.0 \times 10^{-6} \text{ s}^{-1}$ ) but accelerates in aprotic media and is especially fast in solvents such as dimethyl sulfoxide and hexamethylphosphoramide. In the latter solvent, the rate constant is faster than in water by nearly a factor of  $10^8$ .



When dissolved in water, the poly(crown ether)/P18C6 is a tightly coiled macromolecule of low intrinsic viscosity and with an inverse temperature solubility. It behaves as a neutral micelle or polysoap and was shown to strongly interact hydrophobically with organic anions such as picrate or methyl orange.<sup>6</sup> Addition of P18C6 to an aqueous solution of I causes the carboxylate to bind to the neutral polymer, and it was found that in the bound state its reactivity is 2300 times that in water<sup>2</sup> and close to that found by Kemp et al.<sup>4</sup> for the decarboxylation of I in benzene. Addition of crown-complexable cations such as Cs<sup>+</sup> ions further enhances both the binding and reactivity of the carboxylate. The rate constant of substrate I bound to a Cs<sup>+</sup> charged P18C6 was found to be 14 000 times higher than that of the free carboxylate in water.

In most instances where crown ethers have been utilized to catalyze organic reactions,<sup>7,8</sup> the rate acceleration results from anion activation due to ligand interaction with the cation. The interaction either forces the reactant to transfer to a more reactive medium (phase transfer catalysis), or it leads to a breakup of unreactive aggregates, to an increase in the ion pair distance (e.g., formation of crown complexed loose ion pairs) or to a higher fraction of reactive free ions. To facilitate recovery of the crown ethers after a reaction, materials have been developed with crown ligands anchored to insoluble polymeric networks.<sup>9,10</sup> However, attaching these ligands to a macromolecule is known to modify their cation binding properties, especially in systems where the cations form stable 2:1 crown-cation complexes. This in turn could affect their properties as anion activators, particularly in reactions where crown interactions result in ion pair separation. To determine the polymeric effect, the decarboxylation of the potassium salt of I was studied in benzene in the presence of 4'-methylbenzo-18-crown-6 and the results were compared with those obtained in the presence of P18C6 and styrene copolymers of 4'-vinylbenzo-18-crown-6. Without crown, the potassium carboxylate in benzene is expected to be a very tight ion pair, and crown complexation is likely to make it less tight and accelerate its decomposition. The reaction itself is well suited for this type of study since it is unimolecular and yields a product than can easily be monitored spectrophotometrically. The results reveal that the decomposition rate constant of the

crown-complexed salt in benzene is much higher than that reported for the tetramethylquadinium salt of this carboxylate.<sup>4</sup>

## Experimental Section

**Materials.** The synthesis of 6-nitrobenzisoxazole-3-carboxylic acid (abbreviated as acid-I) has been reported.<sup>2,13</sup> The preparation of 4'-methylbenzo-18-crown-6 (MB18C6) and of 4'-vinylbenzo-18-crown-6 as well as the conversion of the vinyl monomer to its homopolymer and its copolymers with styrene has also been described.<sup>11,14,15</sup> The number average molecular weights of the polymers as determined by high-speed membrane osmometry were approximately 40 000. Copolymer compositions were determined by <sup>1</sup>H NMR and were found to be close to the composition of the starting monomer feed, the styrene-vinylbenzocrown ether reactivity ratios being close to unity. Cryptand 2.2.2 and 18-crown-6 were commercial products from Merck and Aldrich, respectively. Spectroscopic grade benzene was stored over fresh sodium wire.

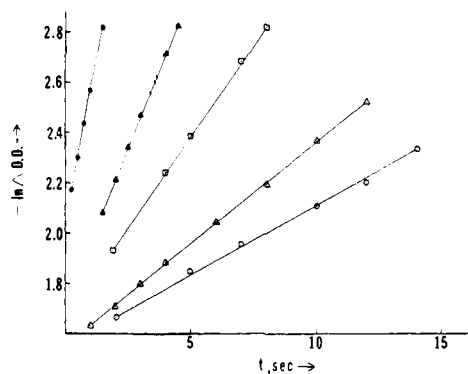
**Solutions.** Potassium 6-nitrobenzisoxazole-3-carboxylate is insoluble in benzene and, therefore, was prepared just prior to the kinetic measurements from a solution of acid I in benzene and a benzene solution of potassium *tert*-butoxide (Aldrich) containing the appropriate crown compound. Immediately after mixing the ensuing decarboxylation reaction was monitored spectrophotometrically. The *tert*-butoxide solution was prepared under nitrogen by dissolving the solid base in benzene and carefully filtering off any insoluble material. A clear stock solution of about 0.1 M was prepared. The *tert*-butoxide concentration was measured by shaking a 5-mL aliquot of the solution with 10 mL of water and measuring the pH of the aqueous solution with an Orion 801 pH meter standardized with two buffer solutions of pH 7.00 and 12.45. Reproducible results were obtained by following this procedure, but it was necessary to refilter the *tert*-butoxide stock solution prior to a new series of kinetic runs and to redetermine its concentration.

**Kinetic Measurements.** Reactions with half-lifetimes above 5 s were measured in a Cary 15 spectrophotometer. An optical cell containing 2 mL of the carboxylic acid I solution of known concentration was placed in the cell compartment and, with the spectrophotometer running, a known amount of a *tert*-butoxide-crown ether mixture was rapidly injected by means of a syringe. Mixing was complete in about 1 s, as indicated by the stability of the recorder pen. The reaction was monitored at the absorption maximum of the product, 2-cyano-5-nitrophenoxide, which lies between 400 and 460 nm, depending on the counterion and crown ether. The extinction coefficient was found to be 3600, but varies slightly with the counterion. The reaction is quantitative, the final optical density of the product spectrum being within 5% of the value calculated from the starting acid I concentration. For reactions with half-lifetimes less than 5 s, a Durrum stop-flow spectrophotometer was used. Oscilloscope traces were recorded on Polaroid film after scale expansion; time scale and noise settings were manipulated to produce a smooth, reproducible curve. First-order rate constants were calculated from the expression  $k = (1/t) \ln a_\infty / (a_\infty - a_t)$  where  $a_t$  and  $a_\infty$  refer to the optical densities at times  $t$  and  $t = \infty$ , respectively.

## Results

The mixing of acid I and crown complexed potassium *tert*-butoxide produces instantaneously potassium 6-nitrobenzisoxazole-3-carboxylate as demonstrated by the results of Table I and Figures 1 and 2. The decarboxylation reaction, followed to completion, is perfectly first order, with correlation coefficients usually better than 0.999. The rate constants are independent of acid I, *tert*-butoxide, and crown concentration (Table I) as long as crown ether and base are in excess. Excess crown is needed to keep the potassium carboxylate solubilized. The conversion to the phenoxide product is quantitative. It was also ascertained that the order of mixing does not affect the reaction, i.e., mixing the crown ether first with acid I gives identical results as when the crown is present in the butoxide solution. Also, small amounts of *tert*-butyl alcohol present in the solution after mixing acid I and *tert*-butoxide did not interfere with the decarboxylation reaction.

Rate constants calculated from first-order plots of runs



**Figure 1.** Plots of  $-\ln \Delta OD$  ( $\Delta OD = a_{\infty} - a_t$ ; see Experimental Section) vs.  $t$  for the decarboxylation of potassium carboxylate I ( $5 \times 10^{-4}$  M) in the presence of MB18C6 ( $5 \times 10^{-3}$  M) and  $t$ -BuOK ( $2 \times 10^{-3}$  M). (●) 37.5, (▲) 30.5, (□) 25.0, (△) 19.9, (○) 16.3 °C.

**Table I.** Decarboxylation Rate Constant of Potassium 6-Nitrobenzoxazole-3-carboxylate in Benzene at 25 °C as Function of the Concentrations of Acid I,  $t$ -BuOK, and MB18-crown-6

acid I $\times 10^4$ , M	[ $t$ -BuOK] $\times 10^3$ , M	[MB18C6] $\times 10^3$ , M	$k$ , $s^{-1}$
1.25	2.0	10	0.150
4.62 <sup>a</sup>	2.0	10	0.142
5.07	1.0	10	0.141
4.32	2.0	5	0.136
3.20	4.0	10	0.161
4.64	1.0	5	0.138
5.90	2.0	2.5	0.132
4.99 <sup>a</sup>	2.0	10	0.145

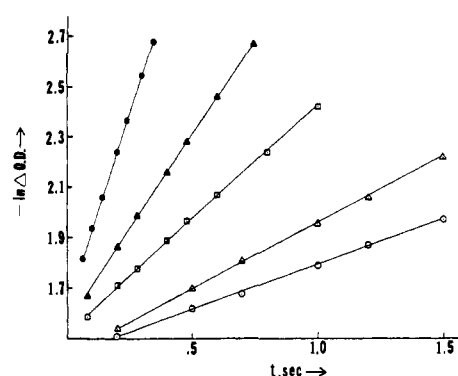
<sup>a</sup> The solutions of these two runs came from different stock solutions, and one run was carried out in the Durrum stop-flow, the other in the Cary spectrophotometer. Note the good reproducibility of the rate constants.

carried out at different temperatures in the presence of MB18C6 and P18C6 (Figures 1 and 2) are listed in Table II. Results are also included for experiments carried out with cryptand 2.2.2 as cation binding ligand. The plots of Figures 1 and 2 should give the same intercept since the experiments were carried out at the same acid I concentration, and conversion was complete (the intercept is determined by the final optical density of the product). However, most runs were carried out with the Durrum stop-flow spectrophotometer, and the time  $t = 0$  was taken somewhat arbitrarily, usually about 1 s after mixing. This, of course, does not affect the calculation of the rate constant.

A series of experiments was carried out with copolymers of styrene and 4'-vinylbenzo-18-crown-6, and the results, shown in Table III, compared with the decarboxylation rate constants measured in the presence of methylbenzo-18-crown-6, 18-crown-6, and cryptand 2.2.2 (the abbreviation SP18C6 (1.65%) denotes a copolymer of styrene with 1.65 mol % of vinylbenzo-18-crown-6 as determined by <sup>1</sup>H NMR). In each case the absorption maximum of the product was carefully recorded and their values are also listed in Table III. Activation energy plots are depicted in Figure 3. Although the temperature range is rather narrow, correlation coefficients of the plots are better than 0.999; hence, the activation parameters appear to be reasonably reliable.

## Discussion

Crown ether catalyzed reactions under homogeneous, liquid-solid and liquid-liquid (phase transfer) conditions have been extensively reported over the past 10 years, including reactions involving alkoxides and carboxylates.<sup>8</sup> In our system



**Figure 2.** Plots of  $-\ln \Delta OD$  vs.  $t$  for the decarboxylation of potassium carboxylate I ( $5 \times 10^{-4}$  M) in the presence of P18C6 ( $7.5 \times 10^{-3}$  M) and  $t$ -BuOK ( $2 \times 10^{-3}$  M). (●) 37.1, (▲) 29.9, (□) 25.0, (△) 20.0, (○) 16.8 °C.

**Table II.** Temperature Dependence of the Decarboxylation Rate Constant of Potassium 6-Nitrobenzoxazole-3-carboxylate in Benzene in the Presence of MB18C6, P18C6, and Cryptand 2.2.2, Respectively<sup>a</sup>

MB18C6		P18C6		cryptand 2.2.2	
$T$ , °C	$k$ , $s^{-1}$	$T$ , °C	$k$ , $s^{-1}$	$T$ , °C	$k$ , $s^{-1}$
16.3	0.0548	16.8	0.363	18.0	2.25
19.9	0.0826	20.0	0.525	25.0	4.78
25.0	0.141	25.0	0.90	30.5	8.72
30.5	0.247	29.9	1.50	35.6	14.7
37.5	0.515	37.2	3.06		

$\Delta H^\ddagger = 18.2$  kcal/mol    $\Delta H^\ddagger = 18.1$  kcal/mol    $\Delta H^\ddagger = 19.5$  kcal/mol  
 $\Delta S^\ddagger = 1.47$  eu    $\Delta S^\ddagger = 1.65$  eu    $\Delta S^\ddagger = 9.9$  eu

<sup>a</sup> [Acid I] =  $5 \times 10^{-4}$  M; [ $t$ -BuOK] =  $2 \times 10^{-3}$  M; [MB18C6] =  $5 \times 10^{-3}$  M; [P18C6] =  $7.5 \times 10^{-3}$  M; with the cryptand all concentrations were half of those given for the MB18C6 runs.

the crown first activates the postassium *tert*-butoxide, which in benzene is reported to be a tetrameric species<sup>16</sup> and which becomes highly reactive in the presence of a crown compound.<sup>8,17</sup> This facilitates the rapid formation of the potassium carboxylate I, which immediately becomes crown complexed. In the absence of crown the mixing of acid I with *tert*-butoxide slowly produces a precipitate. It was not possible to obtain the rate constant of the noncomplexed, tight potassium ion pair, but it is probably much lower than that found for the crown-complexed carboxylate.

Few kinetic data are available on crown-activated carboxylate reactions. Most observations are restricted to a comparison between nucleophilic displacement and elimination reactions pertaining to alkyl and aryl halides<sup>8,18</sup> and the synthetic aspects of carboxylate attack on carbonyl compounds.<sup>19</sup> Also reported has been the effect of crown structure on the half-lifetime of the reaction between potassium acetate and benzyl chloride.<sup>20</sup> Of relevance to our work is the unimolecular decomposition of sodium 3-(fluorene-9-ylidene)-2-phenylacrylate which in dry THF at  $-45$  °C yields a carbanion intermediate that on quenching with water is protonated to neutral products.<sup>21</sup> Addition of dibenzo-18-crown-6 accelerated the decarboxylation by at least a factor of  $10^3$  and possibly a factor of  $10^5$ . Hunter et al. proposed that the  $Na^+$  ion stabilizes the charge-delocalized transition state leading to the carbanionic intermediate to a lesser extent than the tight carboxylate ion pair. Addition of crown would then form a crown separated ion pair, and greatly reduce the cation stabilization of the carboxylate, resulting in a strong rate acceleration.

A similar rationale was advanced by Kemp et al. for the slow decarboxylation of I in protonic solvents,<sup>3-5</sup> and the effect of

**Table III.** Effect of Styrene-Vinylbenzo-18-crown-6 Copolymers on the Decarboxylation Rate Constant of Potassium 6-Nitrobenzoxazole-3-carboxylate in Benzene at 25 °C<sup>a</sup>

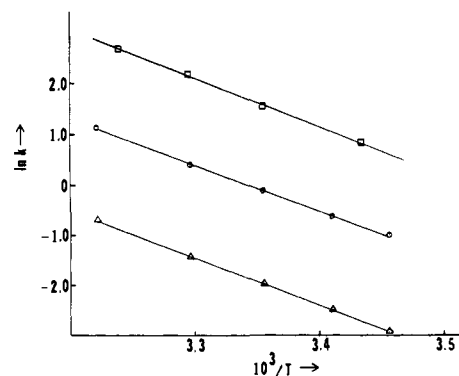
run	crown	$k$ , s <sup>-1</sup>	$\lambda_m$ <sup>b</sup>
1	SP18C6 (1.65%)	0.128	444
2	SP18C6 (5.5%)	0.126	445
3	SP18C6 (9.1%)	0.169	446
4	SP18C6 (19.1%)	0.214	447
5	SP18C6 (47.9%)	0.540	448
6	P18C6	0.90	450
7	MB18C6	0.141	444
8	18-crown-6	0.260	445
9	cryptand 2.2.2	4.78	454

<sup>a</sup> Acid I =  $5 \times 10^{-4}$  M; [*t*-BuOK] =  $2 \times 10^{-3}$  M; [crown] =  $5 \times 10^{-3}$  M. For runs 1, 2, and 9 all concentrations were four times lower.  
<sup>b</sup> Absorption maximum in benzene of the crown-complexed product, potassium 2-cyano-5-nitrophenoxide.

dipolar aprotic solvents such as Me<sub>2</sub>SO and HMPA appear to resemble the kind of solvent effects discussed by Parker<sup>22</sup> for anionic reactants. In the work of Kemp and Paul the counterion was tetramethylguanidinium (TMG<sup>+</sup>), and their rate constants obtained in benzene and ether solvents were believed to be lower bounds due to possible ion pairing.<sup>4</sup> From an inspection of our data, this appears to be indeed the case. For example, the rate constants of the crown-complexed ion pairs in benzene are in the order of 0.1–1.0 s<sup>-1</sup> (Table III), which is 30–300 times higher than the value  $k_{25^\circ\text{C}} = 0.003$  s<sup>-1</sup> reported for the TMG<sup>+</sup> salt.<sup>4</sup>

It has been stated that the high reactivity of nucleophiles in the presence of crown ethers is a result of the formation of crown-complexed separated ion pairs.<sup>8,21</sup> Such ion pairs have indeed been observed, for example, on addition of crown ethers to carbanions such as fluorenyl salts<sup>23</sup> and picrate salts.<sup>24</sup> However, spectral investigations on the structure of crown-ion pair complexes have revealed that in low polarity solvents such as diethyl ether and chloroform and certainly also in benzene, crown-complexed tight ion pairs are often the only stable species.<sup>14,24,25</sup> This is especially the case when dealing with more charge-localized anions such as carboxylates or phenoxides. In such systems the crown only complexes externally to the tight ion pair, and penetration of the cation into the crown cavity is prevented by the high electrostatic interaction energy between the two ions, especially if the solvent is not effective in stabilizing the enlarged loose ion pair dipole or in interacting with the cation as it protrudes from the crown cavity (i.e., formation of solvates such as A<sup>-</sup>, C, M<sup>+</sup> . . . S will favor the crown separated ion pair). Even the more charge-delocalized picrate salts, when complexed with MB18C6 or 18C6, have optical spectra not very different from that of the tight ion pairs. For example, the respective absorption maxima of the Li, Na, K, and Cs salts of picrate in dioxane are 335, 344, 348, and 351 nm,<sup>26</sup> while the 1:1 complexes of potassium picrate with MB15C5, MB18C6, and 18C6 are 353, 357, and 357 nm, respectively.<sup>26</sup> The cryptand complex of potassium picrate in dioxane absorbs at 376 nm, close to that reported for the loose ion pair of this salt.<sup>24,25</sup> Hence, the MB18C6- or 18C6-complexed potassium carboxylate ion pair in benzene can still be considered as a rather tight ion pair, the COO<sup>-</sup> . . . K<sup>+</sup> interionic distance being enlarged on complexation with these crown ethers by possibly 0.5–1 Å.

It should be stressed that even an extension of the ionic bond by 0.5 Å may profoundly affect the ion pair reactivity as a result of anion destabilization. Assuming a reasonable interionic distance of 3 Å in the tight RCOO<sup>-</sup>,K<sup>+</sup> ion pair in benzene, and taking a microscopic dielectric constant of 2, a loss of Coulomb interaction energy of 8 kcal/mol is calculated to

**Figure 3.** Activation energy plots for the decarboxylation of potassium 6-nitrobenzoxazole-3-carboxylate (I) in benzene. (Δ) MB18C6; (○) P18C6; (□) cryptand 2.2.2.

occur on stretching the interionic ion pair distance by 0.5 Å, and 13.5 kcal/mol if the distance is increased by a total of 1 Å. Assuming the same  $\Delta S^\ddagger$ , a change of 10 kcal/mol in  $\Delta H^\ddagger$  changes the rate constant by a factor 10<sup>7</sup>. Of course, the transition state is also destabilized, but, since it is more delocalized than the carboxylate, the effect is expected to be considerably smaller. It may also be recalled that the spectral shifts in fluorenyl and picrate salts as a function of the interionic ion pair distance are relatively large at short distances. When in a tight picrate ion pair Li<sup>+</sup> is replaced by Na<sup>+</sup>, the 0.30 Å increase in ionic radius causes the  $\lambda_m$  in THF to shift from 339 to 351 nm<sup>24</sup> and in dioxane from 334 to 344 nm. A further increase by 0.67 Å to Cs<sup>+</sup> changes  $\lambda_m$  to 362 (THF) and 351 nm (dioxane), respectively. Hence, small changes in the interionic distance of a tight ion pair can induce large changes in the properties of the anion such as their spectra and reactivities. It is, therefore, not necessary or justified to invoke formation of crown-complexed loose ion pairs to rationalize large rate effects on addition of crown ethers (loose ion pairs are used here in the context of an equilibrium between two distinguishable crown-ion pair complexes). Even on addition of cryptand it is doubtful whether in benzene the K<sup>+</sup> is fully sequestered by the bicyclic ligand. The cryptand is known to assume conformations such that a localized anionic charge can approach the bound cation quite closely.<sup>27</sup> Nevertheless, the cryptated ion pair should be considerably looser than the crown-complexed tight ion pairs, and this is reflected in the 20–40-fold increase in rate constant (Tables II and III) when MB18C6 or 18C6 is replaced by cryptand. The higher interionic distance in the cryptated carboxylate ion pair cannot be observed directly in the spectrum, but the spectrum of the product, i.e., the cryptated phenoxide, has a  $\lambda_m$  of 454 nm compared with only 444 nm for the MB18C6-complexed product (Table III).

It is of interest to note that the rate constant of the cryptated ion pair in benzene,  $k_{25^\circ\text{C}} = 4.78$  s<sup>-1</sup>, is nearly identical with that found for the (presumably free) carboxylate anion in Me<sub>2</sub>SO,  $k_{25^\circ\text{C}} = 5.0$  s<sup>-1</sup>, and 1000 times higher than that reported for the TMG<sup>+</sup> salt in benzene,  $k_{25^\circ\text{C}} = 0.003$  s<sup>-1</sup>.<sup>4</sup> If a free ion could be formed in benzene, it probably would have an even higher reactivity than the cryptated ion pair. This leads to the conclusion that the TMG<sup>+</sup>-carboxylate salt is a rather tight ion pair in benzene, and this may also be the case in ether type solvents such as dioxane. It raises the question as to what extent the solvent effects on this reaction follow the pattern described by Parker for anionic reactants in general.<sup>4,22</sup> Certainly ion pairing appears to play a dominant role in the less polar solvents.

The high reactivity of the cryptated and, therefore, rather loose ion pair of I in benzene also sheds more light on our data

for the decarboxylation of I bound to P18C6 in water.<sup>2</sup> The decarboxylation rate constants were found to be  $0.0069 \text{ s}^{-1}$  for I bound to neutral P18C6 and  $0.042 \text{ s}^{-1}$  for I bound to Cs<sup>+</sup> charged P18C6. Based on the spectra of P18C6 bound picrate anions in water,<sup>6</sup> and the rate constant of the TMG<sup>+</sup> salt of I in benzene,<sup>4</sup> it was suggested that the bound carboxylate is probably embedded in the inner core of the tightly coiled P18C6 macromolecule, surrounded by benzene moieties.<sup>2</sup> However, the considerably lower reactivity of the P18C6-bound carboxylate in water as compared with the cryptated carboxylate in benzene suggests that the former species may be present as an ion pair in the polymer domain, or it may still be partially hydrated and close to the polymer-water interphase of the macromolecule.

Anchoring crown ligands to a polymer chain does not change their effect on the decarboxylation rate constant significantly as long as the spacing between crown ligands permits easy access of the carboxylate ion pair to the crown compounds. This is shown by the results obtained for those styrene-crown copolymers which have a low crown content (Table III). The polymer-complexed ion pair will then be similar in structure to the MB18C6-complexed species. However, significant rate increases occur when the crown content of the polymer exceeds 10 mol %, the homopolymer P18C6 showing a rate increase of a factor 7 compared with the monomeric analogue MB18C6. This rate enhancement again may be associated with an increase in the average interionic ion pair distance which could result from the fact that a closer spacing of the crown ligands makes it more difficult for the carboxylate to associate with the crown complexed cation. Some evidence for a larger interionic ion pair distance can be deduced from the gradual bathochromic shift observed for the crown-complexed potassium phenoxide product as the crown content of the polymer increases (Table III).

We also attempted to decompose I in benzene in the presence of the homopolymer and styrene copolymers of 4'-vinylbenzo-15-crown-5. Benzo-15-crown-5 forms 2:1 complexes with K<sup>+</sup>,<sup>24</sup> and the polymers carrying this ligand often form crown separated ion pairs, e.g., with potassium picrate.<sup>25</sup> Such polymers could be even more effective in decomposing the potassium carboxylate. Unfortunately, all of them, including the bis(crown ethers) of benzo-15-crown-5,<sup>24</sup> produced cloudy solutions after adding acid I to the *t*-BuOK-crown mixture.

No activation parameters for the carboxylate decomposition in benzene have been reported, but those measured in Me<sub>2</sub>SO, CH<sub>3</sub>CN, and HMPA reveal that rate accelerations are caused by a decrease in the activation enthalpy  $\Delta H^\ddagger$  from 32 kcal/mol in water to about 23–25 kcal/mol in the dipolar aprotic solvents, the entropy being essentially unchanged at 18–20 eu.<sup>4</sup> In the MB18C6-K<sup>+</sup> carboxylate system in benzene  $\Delta H^\ddagger$  is 18.1 kcal/mol and  $\Delta S^\ddagger$  close to zero (Table II). The very small change in entropy can be expected in an apolar medium such as benzene for a unimolecular decomposition in which charge is conserved. The higher  $\Delta H^\ddagger$  values in the dipolar aprotic solvents as compared with benzene are probably the result of better solvent stabilization of the charge-localized carboxylate in the former solvents. It is not immediately obvious why the increase in rate constant with P18C6 or cryptand as compared with MB18C6 is due to a favorable  $\Delta S^\ddagger$  change rather than to a decrease in  $\Delta H^\ddagger$  (Table II) as would be reasonable to expect if the rate enhancement results from an increase in the interionic ion pair distance. However, in the transition state a new charge is developed at the phenolic oxygen atom. It has been shown in reactions such as the ring opening of ethylene oxide with carbanion and nitranion salts that the cation catalyzes the reaction by interacting with the newly developing charge at the oxygen atom.<sup>28–30</sup> Cryptand or crown complexation to the cation often slows down the reaction in these systems in spite of the larger interionic ion pair distance which

facilitates charge delocalization in the transition state. Which of the two opposing factors is dominant depends on the tightness of the ion pair of the starting material.<sup>30,31</sup> For a localized charge the enlargement of the interionic ion pair distance is usually the dominant factor, while for charge delocalized reactants such as the fluorenyl carbanion it is more important whether the cation can function effectively in its catalyzing role. Also, the complexed cation must be moved to the new anionic site, and this may involve a favorable or unfavorable entropy change depending on the ligand and possible changes in ion pair structure. All these factors make it difficult to give a clear interpretation of the changes in  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  when different ligands are used, and more data are required to solve this problem.

Finally, it should be pointed out that cryptand or a crown ether itself, in the absence of potassium *tert*-butoxide, can also decompose acid I. Cryptand and acid I in benzene form a quaternary ammonium carboxylate which decomposes relatively fast,  $k$  (20 °C)  $\approx 4 \times 10^{-3} \text{ s}^{-1}$ .<sup>32</sup> This is more than a thousand times smaller than the rate constant for cryptated potassium carboxylate, but comparable to the value found for the TMG<sup>+</sup> salt<sup>4</sup> and considerably higher than observed for the salt with triethylamine,<sup>32</sup>  $k$  (20 °C)  $\approx 10^{-4} \text{ s}^{-1}$ . Crown ethers are known to ionize acids such as *p*-toluenesulfonic acid, picric acid, and trifluoroacetic acid in solvents such as 1,2-dichloroethane,<sup>33</sup> but MB18C6 added to acid I in benzene did not produce any decomposition product within 24 h. However, in dioxane there appears to be considerable ionization and formation of the carboxylate, probably because the proton-crown complex can be further stabilized by interaction of the proton with a dioxane molecule. The rate constant at 20 °C in this solvent is in the order of  $10^{-4} \text{ s}^{-1}$ , but the reaction appears to accelerate at higher conversion.<sup>32</sup>

In conclusion, we have shown that crown ethers strongly catalyze the decarboxylation of potassium 6-nitrobenzisoazole-3-carboxylate in benzene. Crown-complexed tight ion pairs are formed in which the interionic ion pair distance is enlarged by probably not more than 1 Å compared with that of the noncomplexed tight ion pair of the carboxylate salt. Further rate enhancements can be achieved by using poly(crown ethers) or a cryptand. The rate constants are much higher than previously found for the tetramethylguanidinium salt in benzene and are comparable with rate constants obtained in dipolar aprotic solvents.

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## Cation Effects on the Equilibrium Acidity of Carbon Acids in Methanol

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**Abstract:** The ratio  $[A^-]/[AH]$  where AH is a carbon acid was examined in methanol at various concentrations of potassium and tetramethylammonium methoxides. The carbon acids were 9-cyanofluorene, 9-carbomethoxyfluorene, *N*-fluorenylidene-fluorene-9-amine, 1,3-diphenylindene, and *N*-methyl-*N*-phenylfluorene-9-carboxamide. All of these compounds with the exception of 9-cyanofluorene were more completely ionized by tetramethylammonium methoxide than by potassium methoxide but none showed as great a sensitivity to this change in cation as did the previously studied fluoradene system. Within the series, the value of  $[MOMe]$  at which cation differentiation was observed varied with carbanion ( $A^-$ ) structure. It is concluded that carbanion-cation interaction can be an important stabilizing influence in methanol but that the magnitude of this effect varies considerably with carbanion structure. An interpretation is made in terms of a competition between hydrogen bonding and ion pairing which is sensitive to charge delocalization in  $A^-$ .

Several investigations have shown that the equilibrium basicity of methoxide at high concentrations is a function of concentration.<sup>1</sup> Streitwieser<sup>1d</sup> has pointed out that the empirical acidity functions used to correlate the effective basicity of methoxide ion with its concentration are dependent to some extent on the indicator acid used to establish the function. In other terms, for the ratio  $\gamma_{A^-}/\gamma_{AH}\gamma_{MeO^-}$  where the  $\gamma$  are activity coefficients, the effect of methoxide concentration on  $\gamma_{A^-}$  cannot be ignored. Schaal and Lambert<sup>1a</sup> have also shown that different acidity functions are obtained using different methoxide salts ( $K^+$ ,  $Na^+$ ,  $Li^+$ ) with potassium methoxide being an effectively stronger base for the indicators of their study. More precisely,  $\gamma_{A^-}/\gamma_{AH}\gamma_{MeO^-}$  is also dependent on the nature of the cation present.

This dependence on  $[MOMe]$  and on  $M$  also extends to kinetic acidity measurements. Cram and co-workers<sup>2</sup> noted a kinetic order of 1.09 for the KOMe-catalyzed racemization of 2-methyl-3-phenylpropionitrile. More O'Ferrall and Ridd<sup>3</sup> showed that, in the NaOMe-promoted methanolysis of chloroform, the second-order rate constant varied with  $[NaOMe]$ . The order in  $[NaOMe]$  can be calculated as 1.3 over the same concentration range as Cram's study (below 0.6 M). The temperature was 60 °C in the latter study and 85 °C in the former. A particularly interesting feature of the More O'Ferrall and Ridd study was the progressive disappearance of this excess order in methoxide when the substrate was changed from chloroform to 1-phenylethyl chloride and then to 1-chloro-3,3-dimethylbutane. Clearly, the change in  $[MOMe]$  cannot be viewed as affecting only  $\gamma_{MeO^-}$ . The effect on  $\gamma_{A^-}$  or  $\gamma^\ddagger$  must also be considered.

More recently, we have shown that the kinetic basicity of methoxide ion in methanol is affected by both  $[MOMe]$  and  $M$  in its reaction with 9-methoxyfluorene.<sup>4</sup> The apparent kinetic order in methoxide for concentrations below 1 M was 1.5 for KOMe and 1.4 for NaOMe at 30 °C. Data for LiOMe and

$Me_4NOMe$  were also provided and showed clearly that the kinetic basicity of methoxide ion in methanol is cation dependent with the basicity order being  $Me_4NOMe > KOMe > NaOMe > LiOMe$ .

The discovery of cation-dependent changes in the visible spectrum of fluoradenide ion,  $FD^-$ , in methanol<sup>5</sup> tends to support arguments<sup>2,6</sup> that the effects described above should be interpreted in terms of ion pairing. When  $FD^-$  is produced by treating fluoradene (FDH) with either  $Me_4NOMe$  or  $CsOMe$ ,<sup>5b</sup> its visible spectrum shows a double maximum characteristic of contact ion pairs.<sup>7</sup> (For comparison,  $KO-t-Bu$  in *t*-BuOH also produces the double maximum.) We also observed<sup>5b</sup> that the equilibrium basicity of  $Me_4NOMe$  toward FDH is greater than that of potassium methoxide by a factor of 20–25 between 0.1 and 1 M. It seemed important to establish whether the tendency to form ion pairs could be observed for other carbanions or whether we had happened upon a unique system. To do this we tried to select carbon acids of differing structure which were sufficiently similar to fluoradene in acidity that ionization could be measured under the conditions of our previous study. We chose five compounds and examined both spectra and extent of ionization for KOMe and  $Me_4NOMe$  solutions in methanol.

### Results

**9-Cyanofluorene (CFH)** is essentially completely ionized at  $[MeO^-]$  greater than 0.03 M. The carbanion,  $CF^-$ , absorbs in the visible region at 410 nm with  $\epsilon_{max}$  2120.<sup>8</sup> The shape of the spectrum and the  $\lambda_{max}$  are unaffected by changes in  $[MOMe]$  or by changing  $M$  from  $K$  to  $Me_4N$ . As it was also found that the spectral characteristics of this carbanion are not affected by using potassium *tert*-butoxide in *tert*-butyl alcohol for its generation, it is clearly not possible to use visible spectroscopy to determine ion pairing in this case.

We also investigated the dependence of  $[CF^-]/[CFH]$  on