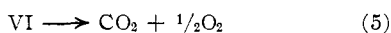
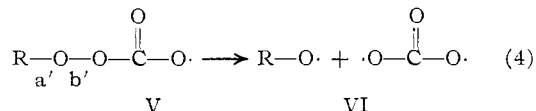
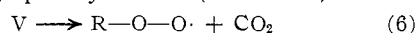


between reaction 1 and 2, it then can be concluded that the first step of the decomposition is represented by reaction 1, and that the radical V is only partially scavenged by the *t*-stilbene.

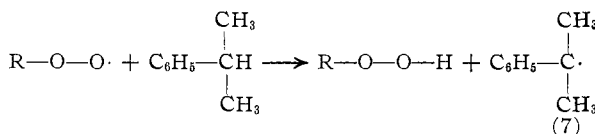
Having established that the first step of the reaction involves the cleavage of one bond, the peroxidic bond a, it remains to ascertain which bond cleaves in the second step. Cleavage of the other peroxidic bond, a', would lead to the *t*-butoxy radical and the species CO₃, which might then decompose into carbon dioxide and oxygen (reactions 4 and 5). Cleavage of bond b', on the



other hand, would lead directly to carbon dioxide and the *t*-butyl peroxy radical (reaction 6).



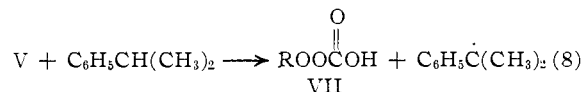
Experiments conducted in cumene establish the latter to be the case. In cumene, the rate is unchanged, indicating no change in mechanism, but it is possible to trap the *t*-butyl peroxy radical, which abstracts a hydrogen atom from the cumene to give *t*-butyl hydroperoxide. The *t*-butyl hydroperoxide was isolated and characterized as its



p-nitroperbenzoate derivative. The isolation of *t*-butyl hydroperoxide demonstrates that the peroxidic bond, a', remains intact during the decomposition.

One further possibility had to be ruled out to establish the validity of this conclusion. It is

conceivable that the *t*-butyl peroxy carbonate radical V might abstract a hydrogen atom from the cumene to give the unstable acid VII and this acid might then decompose to carbon dioxide and *t*-butyl hydroperoxide. In other words, the pathway



by which carbon dioxide is evolved may have been altered by the cumene without affecting the rate of the first step. This can be excluded, however. It was shown that the yield of carbon dioxide from the decomposition in cumene is quantitative. Thus, the acid VII, if formed, must decarboxylate completely. Furthermore, it was found that the effectiveness of stilbene at lowering the carbon dioxide yield was the same in cumene as in *o*-dichlorobenzene. This rules out the acid VII as a carbon dioxide source when cumene is the solvent because, had it been involved, some of the radicals V which in *o*-dichlorobenzene would have added to stilbene and had their subsequent decarboxylation prevented, would have been intercepted by cumene before being scavenged. In short, the stilbene would have been less effective at lowering the yield of carbon dioxide in cumene than in *o*-dichlorobenzene.

It may be concluded that the thermal, free radical decomposition of di-*t*-butyl diperoxy carbonate is a two-step process, in which reaction 1 is followed by reaction 6.

Acknowledgment.—It is a pleasure to acknowledge an unsolicited grant from the Socony Mobil Oil Co., which financed part of this work. Some of the di-*t*-butyl diperoxy carbonate used was prepared by Mr. James Scharphorn. Finally, I wish to acknowledge the frequently useful and always enjoyable discussions of this work with Prof. R. M. Stiles.

[CONTRIBUTION FROM THE SEVERANCE CHEMICAL LABORATORY, THE COLLEGE OF WOOSTER, WOOSTER, OHIO]

The Salt Effect in the Aromatic Nucleophilic Substitution Reaction of 2,4-Dinitrochlorobenzene and Methoxide in Methanol-Benzene

BY JOHN D. REINHEIMER,¹ JOHN THOMAS GERIG AND JOHN C. COCHRAN

RECEIVED AUGUST 8, 1960

The effect of added salts on the rate of reaction of 2,4-dinitrochlorobenzene and alkali metal methoxides in 50% methanol-benzene has been investigated. The rate of reaction follows the order LiOCH₃ < NaOCH₃ < KOCH₃. Potassium salts increase the rate of reaction with all methoxides and lithium salts decrease the reaction rate constant. Sodium salts decrease the rate of reaction with KOCH₃, increase the rate with LiOCH₃ and have little effect with NaOCH₃; NaI does not have the same effect as other sodium salts.

In the previous paper,² the effect of added salts on the rate of reaction of 2,4-dinitrochlorobenzene, hereinafter abbreviated as 2,4-DNCB, and MOCH₃ in methanol was investigated. The salt effects observed were attributed to ion pairing of the

methoxide ion and alkali metal cation. The hypothesis was not regarded as complete, for the accelerating effect of K⁺ salts on KOCH₃ was not explained. A change in dielectric constant of the medium to a lower value should enhance the ion pairing and thus verify or disprove the original hypothesis. A mixture of methanol and benzene was deemed to be a suitable solvent in which to pursue the further investigation of salt effects

(1) This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) J. D. Reinheimer, W. F. Kieffer, S. W. Frey, J. C. Cochran and E. W. Barr, *J. Am. Chem. Soc.*, **80**, 164 (1958).

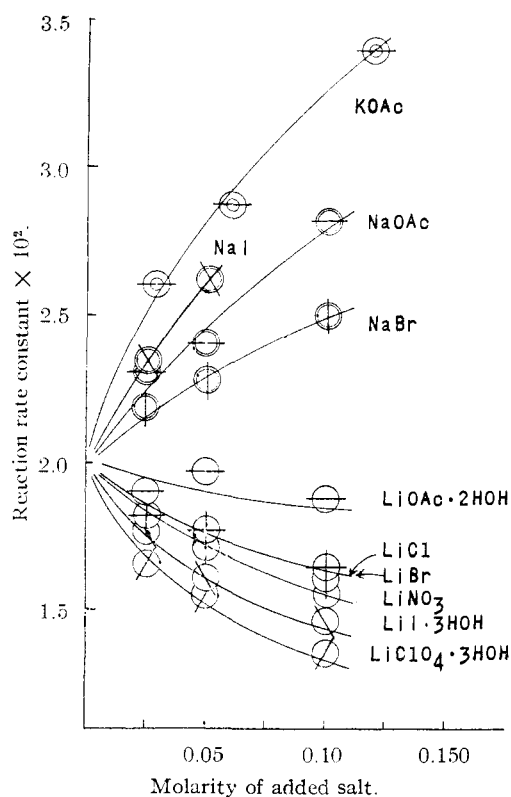


Fig. 1.— LiOCH_3 and 2,4-DNCB in 50% methanol-benzene at 24.90° .

The dielectric constant of the 50% methanol-benzene by volume was calculated by the method of Heppollette and Miller³ to be 23.2.

Experimental

Materials.—The chemicals were purified and dried as in the previous investigation,² with the exception that a temperature of 100° was used instead of 75° for drying. Samples of the salts were dried overnight, about 16 hours. The benzene was Fisher reagent, and was dried for several days over Drierite and then distilled over sodium through a short Vigreux column.

Solutions.—The solvent was prepared by placing 1 liter of methanol in a 2-liter volumetric flask, and diluting to the mark with benzene. This solvent was used to prepare the 2,4-DNCB solution. Solutions of MOCH_3 were prepared by pipeting 20 ml. of a methanolic solution of the alkali metal methoxide into a volumetric flask and pipeting 20 ml. of benzene and then diluting to the mark with the benzene-methanol solvent. This procedure was followed because detection of an end-point was easier in the homogeneous solvent than in the mixed solvent that resulted when the base was added to water.

Procedures.—Precautions and procedures were similar to the previous experiment. Titration of the samples in the mixed solvent was more difficult than in methanol. The samples were pipeted into a stopping solution which contained 5 ml. of standard acid and 30 ml. of water. This mixture, with its benzene layer, was titrated to an approximate end-point with NaOH and a cresol red indicator. The flask was then stoppered and shaken vigorously and NaOH added between shakings until the color of cresol red in basic solution persisted for 100 vigorous shakes. This was a tedious and physically wearing procedure, but there was considerably more scatter in the graphs when the shaking was omitted. Practically, these end-points were still not as good as those obtained in homogeneous solution,⁴ so

(3) R. L. Heppollette, I. R. Lantzke and J. Miller, *Austral. J. Chem.*, **9**, 299 (1956).

(4) A referee asked why this tedious method was used. First, the entire sample could be titrated, with no problems of incomplete sepa-

ration of the methanol, water and benzene layers. If the shaking were omitted, an apparent end-point that occurred 0.1–0.2 ml. before the permanent end-point given by shaking was the result. This apparent end-point faded rapidly. Heppollette and Miller used a mixed indicator of brom cresol green and methyl red, and reported that "Acid-base titration end-points were difficult to observe precisely in benzene-containing solvents without utmost care."

Results

This investigation was divided into three parts: the effect of added salts upon the reaction of (1) LiOCH_3 on 2,4-DNCB, (2) NaOCH_3 on 2,4-DNCB, and (3) KOCH_3 on 2,4-DNCB. In all reactions, the $[\text{MOCH}_3] = [\text{2,4-DNCB}] = 0.025\text{--}0.031\text{ M}$. The solubility of some of the salts, particularly potassium salts, did not permit their use at concentrations higher than 0.10 M. Several of the runs gave a precipitate of KCl toward the end of the experiment. In those cases where this occurred at the start of the run this fact is noted in the tables. The plot of such runs seemed to be normal when compared to other runs in which no precipitate was observed.

The observed rate constants compare favorably with the only other values in the literature. Heppollette, Lantzke and Miller³ gave 3.01×10^{-2} l./mole sec. at 25.2° and our average result was 2.91×10^{-2} l./mole sec. at 24.90° for methanol-benzene. Reproducibility was fair, with the maximum deviation between duplicate runs of $\pm 4\%$ from the average. Since these data were collected at several periods by different investigators and the analytical method was less precise than could be desired, this deviation seems reasonably small. The average deviation for the reaction with no salts added is 0.07 or $\pm 2.4\%$ for NaOCH_3 and 0.07 or $\pm 2\%$ for KOCH_3 .

The data are summarized in Tables I and II and in Figs. 1, 2 and 3. In general, the addition of

TABLE I
REACTION RATE CONSTANT FOR THE REACTION MOCH_3
AND 2,4-DNCB IN METHANOL-BENZENE, 50% (v./v.)
AT 24.90°

Methoxide	Concn., mole/l. ^a	Rate constant $k_2 \times 10^{-2}$, l./mole \times sec.
NaOCH_3	0.01419	2.89; 290
	.025–0.030	2.91 (av.)
	.1064	3.07; 3.11
KOCH_3	.01008	3.26
	.01176	3.35
	.02940	3.43 (av.)
LiOCH_3	.04410	3.69
	.0882	4.14; 4.14
	.00743	2.32; 2.35
	.01574	2.07; 2.11
	.03147	2.00 (av.)
	.1180	1.85; 1.88

^a In all cases, $(\text{MOCH}_3) = (\text{2,4-DNCB})$.

ration of the methanol, water and benzene layers. If the shaking were omitted, an apparent end-point that occurred 0.1–0.2 ml. before the permanent end-point given by shaking was the result. This apparent end-point faded rapidly. Heppollette and Miller used a mixed indicator of brom cresol green and methyl red, and reported that "Acid-base titration end-points were difficult to observe precisely in benzene-containing solvents without utmost care."

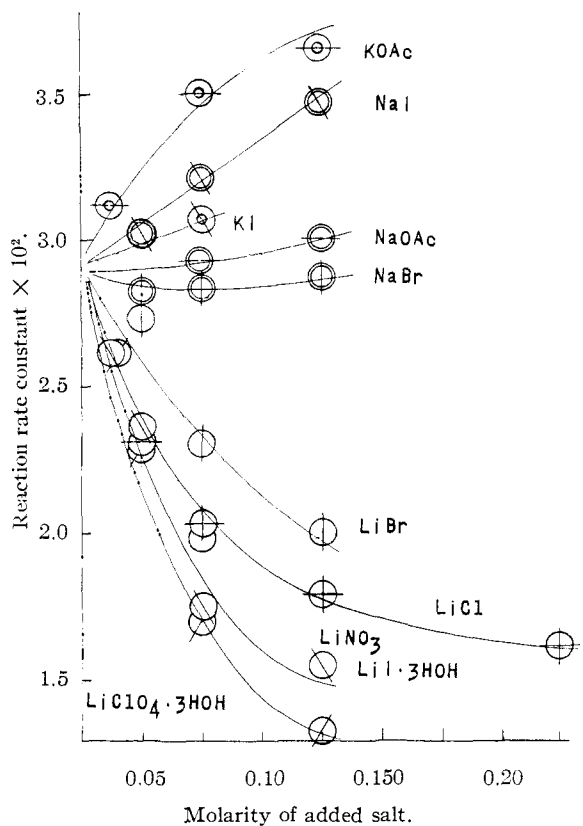


Fig. 2.— NaOCH_3 and 2,4-DNCB in 50% methanol-benzene at 24.90° .

lithium salts caused a substantial decrease in rate constant, but sodium salts increased or decreased the rate constant depending on MOCH_3 . Sodium iodide always caused a rate increase, but the other two sodium salts, sodium acetate and sodium bromide, caused rate decreases with KOCH_3 , little change with NaOCH_3 and rate increases with LiOCH_3 . Potassium salts caused an increase in rate constant, no matter what MOCH_3 was used.

Comparison with previous results in methanol shows that the salts are more effective in methanol-benzene than in pure methanol. Thus, ΔK_2 for 0.10M KOAc is 25% for methanol and 60% in methanol-benzene with LiOCH_3 ; ΔK_2 for 0.10 M $\text{LiClO}_4 \cdot 3\text{HOH}$ was 14% in methanol and 35% in methanol-benzene with LiOCH_3 . When KOCH_3 is used, ΔK_2 becomes greater; for 0.10 M $\text{LiI} \cdot 3\text{HOH}$, ΔK_2 is 0.5×10^{-2} l./mole sec. or 18% in methanol and 1.7×10^{-2} l./mole sec. or 50% in methanol-benzene. These figures are illustrative for those salts which have relatively large ΔK_2 . Salts which had little or no effect on the rate constant in methanol also have little effect in methanol-benzene.

Several salts have altered their relative effectiveness when the solvent was changed. Thus, NaI had little effect in methanol, but has a rate-increasing effect in methanol-benzene; NaOAc, which accelerated the reaction in methanol with all MOCH_3 , was found to accelerate the reaction with LiOCH_3 but to have little effect on potassium or sodium methoxide.

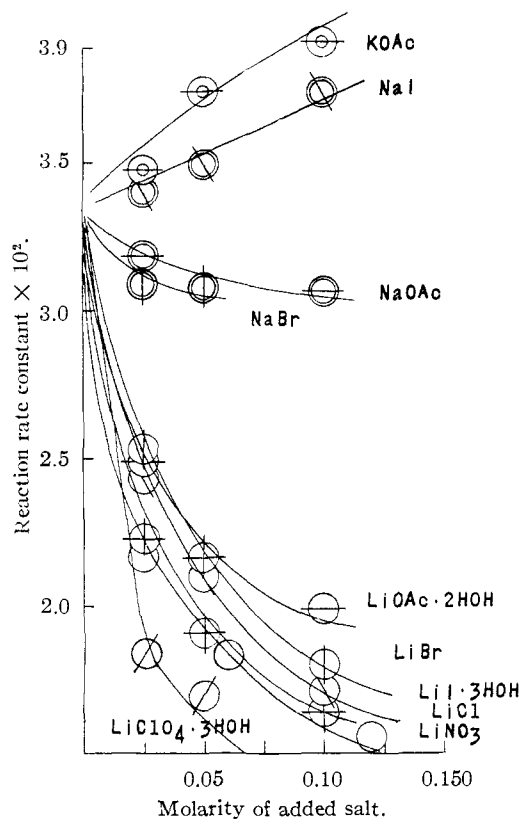
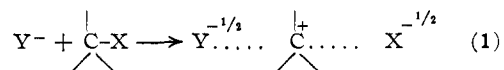


Fig. 3.— KOCH_3 and 2,4-DNCB in 50% methanol-benzene at 24.90° .

Discussion

The observed data do not seem to fit existing theories, so that another explanation for the salt and solvent effects is required. If the dielectric constant of the solvent is decreased for the reaction



the reaction rate is predicted to show a slight increase.^{5a} The observed rate constant changes from 2.60×10^{-2} to 2.91×10^{-2} for the reaction of 2,4-DNCB and NaOCH_3 , from 2.80×10^{-2} to 3.43×10^{-2} for KOCH_3 , and from 2.40×10^{-2} to 2.00×10^{-2} l./mole sec. for LiOCH_3 when the solvent is changed from methanol,² $D = 32.6$, to 50% methanol-benzene, $D = 23.2$ (the concentrations of the three methoxides are nearly equal, and are 0.0280 M). The change in solvent cannot be rate increasing on the one hand and rate decreasing on the other hand if the transition state for the reaction is the same for all three methoxides. A similar argument may be applied to the salt effects, which are expected to be qualitatively similar to the solvent effects.^{5b} In a reaction such as 1 the addition of salts should stabilize the reagent, Y^- , more than the dispersed charge in the transition state, and result in a small rate decrease when neutral salts are added to the reaction mixture. This cannot be the entire explanation, for the sodium and potassium salts have rate-increasing effects, while the lithium salts cause a rate decrease.

(5) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953: (a) p. 347; (b) p. 362.

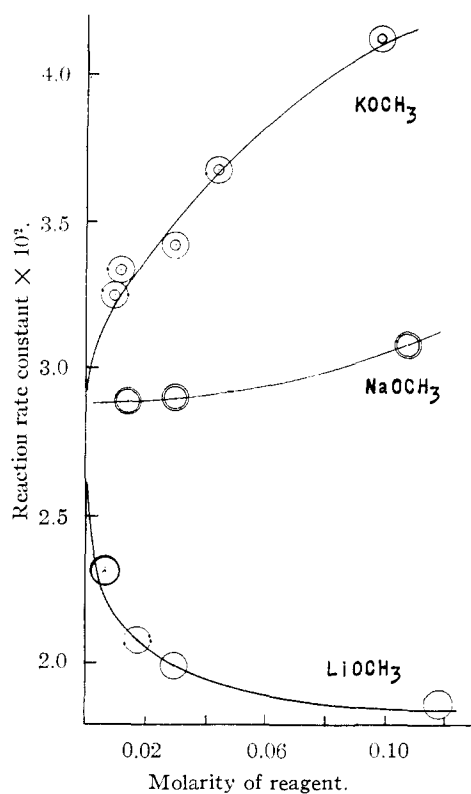


Fig. 4.— MOCH_3 and 2,4-DNCB in 50% benzene-methanol at 24.90° .

The data in Table I and Fig. 4 indicate the effect of ionic strength on the reaction rate constant when the ionic strength is varied by changing the initial concentration of the reactants. The data in Table II and Figs. 1, 2 and 3 are similar, but have the complication that two anions and two cations are present. It seems clear that the same explanation can be applied to the entire body of data, so the following discussion is limited to the simple case of the changed ionic strength by means of changed initial concentration of the methoxide ion.

Two hypotheses, both of which are based on the ideas of ion pairing, may be considered. Both utilize the concept that ion pairing is more extensive in a solvent of lower dielectric constant; hence salt effects are enhanced in the mixed solvent as compared to pure methanol. One involves the idea that the free methoxide ion and the ion pair formed by the alkali metal ion and the methoxide ion are both reactive species.² Acree⁶ first advanced this hypothesis, and recently Brändstrom⁷ has reinvestigated this concept, using modern electrochemical techniques and recalculating data which were available in the literature.

Brändstrom's formulation is

$$\frac{d\phi}{dt} = [2,4\text{-DNCB}]([\text{OCH}_3]k_i + [\text{M}^+\text{OCH}_3]k_{ip}) \quad (2)$$

$$= [2,4\text{-DNCB}][\text{MOCH}_3]_s(\alpha k_i + (1 - \alpha)k_{ip}), \text{ or } \quad (3)$$

$$\frac{d\phi}{dt} = [2,4\text{-DNCB}][\text{MOCH}_3]_s k_{\text{obs}}, \text{ and}$$

$$k_{\text{obs}} = \alpha k_i + (1 - \alpha)k_{ip} \quad (4)$$

(6) S. F. Acree, *Am. Chem. J.*, **48**, 453 (1912).

(7) Arne Brändstrom, *Arkiv Kemi*, **11**, 562 (1957).

TABLE II

RATE CONSTANTS FOR THE REACTION OF 2,4-DNCB WITH MOCH_3 AND ADDED SALTS IN BENZENE-METHANOL, 50% V./V. AT 24.90°

Salt added	Concn. of salt, mole/l.	Rate constant $\times 10^2$, $\text{l.} \times \text{mole}^{-1} \times \text{sec.}^{-1}$		
		LiOCH_3	NaOCH_3	KOCH_3
None		1.99; 2.04	3.01; 2.86	3.42; 3.39
			2.81; 2.90	3.56; 3.35
			2.95; 2.81	3.30; 3.48
	Av.	2.02	Av. 2.91	Av. 3.43
NaBr	0.10	2.44; 2.55	2.88	
	.05	2.29; 2.27	2.84	3.12; 3.03 ^a
	.025	2.18; 2.19	2.83; 2.84	3.06; 3.12 ^a
NaI	.10		3.54; 3.43	3.74
	.05	2.64; 2.60	3.19; 3.24	3.46; 3.52
	.025	2.33; 2.35	3.01; 3.04	3.37; 3.44
NaOAc	.10	2.77; 2.88	3.01 ^b	3.08; 3.04
	.05	2.36; 2.43	2.94	3.05; 3.06
	.025	2.31; 2.31		3.18; 3.17
KI	.05		3.06; 3.11	
	.10	3.36; 3.43 ^c	3.70; 3.58	3.96; 3.83
	.05	2.85; 2.88 ^d	3.52; 3.50	3.70; 3.79
KOAc	.025	2.59; 2.61 ^e	3.08; 3.18 ^f	3.46; 3.48
	.20		1.62	
	.10	1.65; 1.62 ^g	1.80	1.63; 1.66 ^h
LiCl	.05	1.75; 1.79 ^h	2.04	1.93; 1.86 ⁱ
	.025	1.78; 1.86	2.32	2.25; 2.20 ⁱ
	.01		2.66	
LiBr	.10	1.61; 1.63	2.01	1.79; 1.77 ^j
	.05	1.70; 1.73	2.31	2.11; 2.18 ^j
	.025	1.82; 1.82	2.47	2.50; 2.54 ^j
LiI·3HOH	.10	1.43; 1.49	1.50; 1.63	1.73; 1.71
	.05	1.63; 1.59	1.75	2.02; 2.13
	.025	1.78; 1.79	2.38	2.38; 2.48
	.0127		2.63	
$\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$.10	1.33; 1.37	1.33	1.37; 1.38 ^k
	.05	1.56; 1.57	1.71	1.69; 1.68 ^k
	.025	1.62; 1.69	2.30	1.84; 1.82 ^k
	.0125		2.64	
LiOAc·2HOH	.10	1.88; 1.87	2.03	1.97; 1.98
	.05	1.99; 1.95	2.20	2.16; 2.16
	.025	1.89; 1.90	2.36	2.39; 2.49
	.0125		2.52	
LiNO_3	.10	1.55; 1.62	1.78	1.57; 1.57 ^m
	.05	1.74; 1.73	2.00	1.87; 1.78 ⁿ
	.03			2.11; 2.17

^a KBr precipitated in flasks. ^b (NaOAc) = 0.136. ^c (KOAc) = 0.118. ^d (KOAc) = 0.059. ^e (KOAc) = 0.029. ^f (KOAc) = 0.026. ^g (LiCl) = 0.109. ^h (LiCl) = 0.055. ⁱ Precipitation of KCl observed. ^j Precipitation of KBr observed. ^k Precipitation of KClO_4 observed. ^l ($\text{LiClO}_4 \cdot 3\text{HOH}$) = 0.033, ^m (LiNO_3) = 0.118. ⁿ (LiNO_3) = 0.059.

where

k_i = rate constant for methoxide ion

k_{ip} = rate constant for ion pair

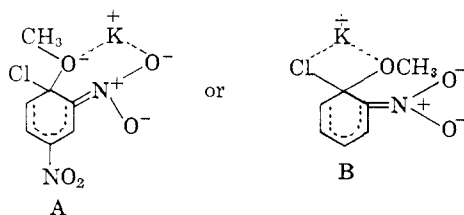
α = degree of ionization of MOCH_3

The degree of dissociation of $(\text{M}^+, \text{OCH}_3^-)$ in methanol-benzene is not available, but the data of Brändstrom for $(\text{M}^+, \text{OC}_2\text{H}_5^-)$ in ethanol are. Since the dielectric constant of ethanol is 24.2 and that calculated for the methanol-benzene solvent is 23.2, the use of his data should not lead to gross errors. Brändstrom gives $\alpha = 0.506$ for LiOC_2H_5 , $\alpha = 0.626$ for NaOC_2H_5 and $\alpha = 0.644$ for KOC_2H_5 at 25° and 0.0313 M . The calculated dissociation constants for the three ethoxides are 1.5×10^{-2} , 3.2×10^{-2} and 3.5×10^{-2} m./l., respectively. These data suggest that LiOCH_3 is the least dissociated of the methoxides. The $(\text{Li}^+, \text{OCH}_3^-)$ ion pair is also expected to be the most stable on the basis of ionic size. This follows from the ease with

which the $-\text{OCH}_3$ can replace a methanol of solvation. Because of its smaller size, the Li^+ makes the H^+ atom on the methanol of solvation somewhat more acidic than the other two cations. Loss of this H^+ to the solution and its subsequent neutralization provides a mechanism by which an *intimate ion pair* is formed readily. However, the ion pair association of Li^+ with other anions may well be less, for the more extensive solvation of Li^+ has increased its apparent size.⁸

If one makes the assumption that $k_{ip} > k_i$ for KOCH_3 , $k_{ip} = k_i$ for NaOCH_3 and $k_{ip} < k_i$ for LiOCH_3 , the data of Fig. 4 may be explained by eq. 2. On the basis of eq. 2, since α decreases as concentration rises, the contribution of k_{ip} ($1 - \alpha$) to k_{obs} becomes larger. From this, it follows that k_{obs} for KOCH_3 will increase, k_{obs} for NaOCH_3 will not change, and k_{obs} for LiOCH_3 will decrease with increasing MOCH_3 concentration.

The implication of eq. 2 is that the transition state for the ion pair (K^+ , $-\text{OCH}_3$) and 2,4-DNCB is more favorable than that of $-\text{OCH}_3$ and 2,4-DNCB. Possibilities of a cyclic intermediate of the type A or B are suggested.

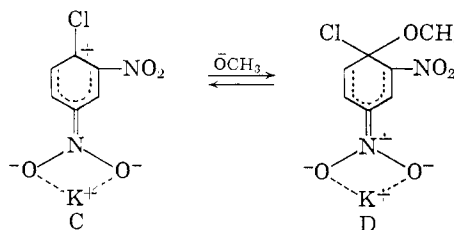


The objection to the analysis of eq. 2 is given by Brändström⁷ as follows: "From the fact that elec-

(8) J. R. Graham, G. S. Kell and A. R. Gordon, *J. Am. Chem. Soc.*, **79**, 2352 (1957).

trons are withdrawn to some extent from the anion in forming the ion pair, it might be expected that the ion pair has a much lower reactivity than the free anion, if there is no steric factor that makes the reaction with the ion pair especially favored." It is to be noted, however, that a cyclic mechanism to account for the reactivity of the ion pair is postulated in several reactions by Brändström.

The second hypothesis is that the rate depends upon the concentration of free methoxide ion and the reactivity of 2,4-DNCB. This assumes that $k_{ip} = 0$. The rate observed should be less than k_i for all concentrations if the reactivity of 2,4-DNCB does not change as the ionic strength increases, for α decreases with all three alkali methoxides. To account for the rate increase with KOCH_3 , some increase in the reactivity of 2,4-DNCB must occur, due to association of the salt with 2,4-DNCB. A possible form is



The association of the K^+ in form C facilitates the attack of the OCH_3^- , or in form D stabilizes the transition state. To account for Fig. 4, the association of M^+ in form C or D would have to be in the order $\text{K}^+ > \text{Na}^+ > \text{Li}^+$. This is the order of ion pairing, as noted by Gordon⁸ for (M^+ , Cl^-).

Acknowledgment.—The authors gratefully acknowledge helpful suggestions by the referees.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY, UPTON, N. Y.]

Slow Proton Transfer Reactions. III. The Mechanism of Acid-catalyzed Aromatic Hydrogen Exchange in 1,3,5-Trimethoxybenzene^{1,2}

BY A. J. KRESGE³ AND Y. CHIANG

RECEIVED FEBRUARY 7, 1961

General acid catalysis has been detected in the exchange of aromatic hydrogen of trimethoxybenzene: rates of loss of tritium from 1,3,5-trimethoxybenzene-2-*t* to seven acids ranging in strength from H_3O^+ to H_2O conform to the Brønsted relation $k_A = 4.72 \times 10^{-2} (K_A)^{0.518}$. This fact is inconsistent with a previously assigned mechanism for aromatic hydrogen exchange; that is, the scheme consisting of reversible formation of a loose complex between proton and aromatic substrate followed by slow intramolecular isomerization of this complex. Instead, general acid catalysis indicates a simple slow proton transfer mechanism for exchange. The loss of tritium from 1,3,5-trimethoxybenzene-2-*t* is not catalyzed by bases. This shows that this proton transfer is not a concerted process, but that reaction takes place in two discrete steps: proton addition to give a phenonium ion followed by proton abstraction to give exchanged trimethoxybenzene. This mechanism, unlike the one first proposed for aromatic hydrogen exchange, is wholly consistent with generally accepted mechanistic schemes for other electrophilic aromatic substitutions.

Introduction

The simplest mechanism which is consistent with all existing data for electrophilic aromatic substi-

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) Presented in part at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 12, 1960. For papers I and II in this series see A. J. Kresge and D. P. N. Satchell, *Chemistry & Industry*, 1328 (1958); A. J. Kresge and Y. Chiang, *J. Am. Chem. Soc.*, **81**, 5509 (1959).

tution, with the sole exception of substitution by hydrogen, is the two-step reaction sequence. In this scheme, either of the steps can be rate-controlling, and perhaps the strongest evidence for this mechanism comes from recent attempts to show which step is slow. For the special case of substitution for hydrogen ($\text{X} = \text{H}$), hydrogen iso-

(3) Department of Chemistry, Illinois Institute of Technology, Chicago 16, Ill.