under reduced pressure, and the contents were analyzed. Nmr and tlc showed no compounds present except **10**.

In another experiment, 0.66 g (0.0025 mol) of **10**, 1.4 g of *tert*-butylamine, and enough benzene to dissolve all the ketone were placed in a test tube and the tube was sealed. After 2 weeks at room temperature, nmr and tlc analysis showed that no reaction had taken place.

Registry No.—**1a**, 33224-47-4; **2a**, 33224-50-9; **2b**, 33224-51-0; **2e**, 33224-52-1; **2e** HCl, 33224-53-2; **2g**, 33224-54-3; **3a**, 33224-55-4; **3a** picrate, 33224-56-5; **3b**, 33224-57-6; **3e**, 33240-01-6; **3f**, 33240-02-7; **3g**, 33240-03-8; **3g** HCl, 33303-98-9; **6a**, 30765-51-6; **6b**, 30765-50-5; **8**, 33240-06-1; **9**, 33240-07-2; **14**, 33240-08-3; **15**, 33240-09-4; **15** HCl, 33240-10-7.

Acknowledgments.—This work was supported in part by a Special Departmental Science Development Award to the Department of Chemistry from the National Science Foundation, No. GU-2054, and in part by a grant from the Nebraska Research Council. One of us (G. G.) wishes to acknowledge financial assistance received in the form of an NSF traineeship and a Monsanto summer fellowship.

Mobile Keto Allyl Systems. XIII.[1] The Kinetics and Mechanism of the Reaction of 2-(α-Halobenzyl)-1,4-dihydro-4,4-dimethyl-1-ketonaphthalene with *tert*-Butylamine[2]

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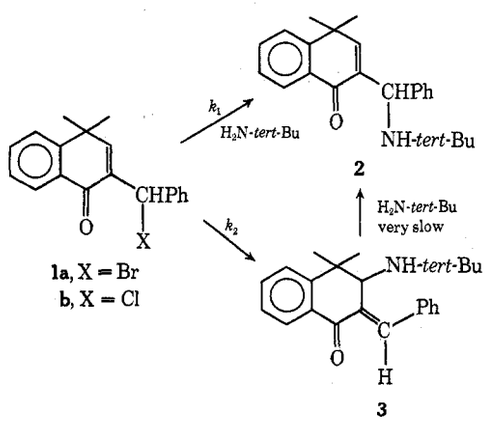
Received June 18, 1971

The title compound **1** was found to react with *tert*-butylamine by parallel reactions which obeyed second-order kinetics, first order in **1** and amine. The reaction yielding direct substitution product **2** is characterized by a large solvent effect ($k_{CH_3CN}/k_{C_6H_6}$ = 124), large leaving group effect (k_{Br}/k_{Cl} = 110), and an activation energy of 15–17 kcal/mol. These data are consistent with a normal SN2 displacement reaction. The reaction yielding abnormal substitution product is characterized by a small solvent effect ($k_{CH_3CN}/k_{C_6H_6}$ = 11), a small leaving group effect (k_{Br}/k_{Cl} = 5.5), and an activation energy of 12–13 kcal/mol. Although not ruling out the possibility of a dipolar intermediate being involved, the data are best interpreted in terms of a variant of an SN2′-type reaction in which the entering of the amino group and the departure of the halogen ion are concerted, but the carbon to nitrogen bond making is running ahead of carbon to halogen bond breaking, and the carbonyl group serves to disperse some of the developing negative charge.

In earlier papers[1,3] in this series it was shown that the halo ketone **1** reacts with *tert*-butylamine to yield two products **2** and **3** by parallel pathways. Compounds **1**, **2**, and **3** were shown to be stable under reaction conditions to rearrangement or decomposition. Because of the stability of these compounds, and because the rearrangement–substitution reaction could be compared with the direct substitution process, it was decided to study the kinetics of the reaction of halo ketone **1** with *tert*-butylamine.



Method.—Compounds **1** and **2** have very similar ir and uv spectra;[3] so both of these methods are unsatisfactory to follow the kinetics of the reaction. Halide titration would give only the overall rate constants $(k_1 + k_2) = k$; so this method is unsatisfactory also. Since the methine proton absorbance of **1** appears near 400 Hz, the methine proton absorbance of **2** appears near 300 Hz, and the methine proton absorbance of **3** appears near 250 Hz[3], it was decided to use nmr to follow the rate of the reaction. The assumption was made that the sum of the concentrations of **1**, **2**, and **3** at any time was a constant and equal to the initial concentration of **1**. Thus, $[1]_0 = [1]_t + [2]_t + [3]_t$ and the individual rate constants k_1 and k_2 could be obtained.

The use of nmr to follow kinetics places certain restrictions on the system. First, large quantities of reactants must be used to get strong enough signals for accurate measurements. Secondly, the method is relatively insensitive; consequently greater errors are introduced when one species is present to a much greater extent than another, as occurs in the beginning and end of a reaction. Lastly, although good correlation may be obtained for the overall rate constant k, the error involved in determining the ratio of **2** to **3** causes a greater error to be introduced in determining the individual rate constants k_1 and k_2. With these restrictions in mind we determined the kinetics of the reaction of **1** with *tert*-butylamine under various conditions. Because of the inaccuracy of the method we have been very cautious about comparing a rate constant we obtained with one obtained by other workers. Instead, we have tried to make comparisons in our system as various factors governing the rate of reaction are changed, such as temperature, solvent, and leaving group.

(1) For paper XII in this series, see G. Glaros and N. H. Cromwell, *J. Org. Chem.*, **37**, 862 (1972).

(2) Presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

(3) N. H. Cromwell and E. M. Wu, *J. Org. Chem.*, **33**, 1895 (1968).

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF 2-(α-BROMOBENZYL)-1,4-DIHYDRO-4,4-DIMETHYL-1-KETONAPHTHALENE (1a) WITH *tert*-BUTYLAMINE IN BENZENE

Temp, °C	[Bromo ketone], mol/l.	[*tert*-Butylamine], mol/l.	k, l. mol^{-1} min^{-1}	k_1, l. mol^{-1} min^{-1}	k_2, l. mol^{-1} min^{-1}
15.0	0.169	0.886	2.3×10^{-5}	4.0×10^{-6}	1.9×10^{-5}
15.0	0.179	0.632	2.3×10^{-5}	4.9×10^{-6}	1.8×10^{-5}
15.0	0.177	0.760	2.0×10^{-5}	3.6×10^{-6}	1.6×10^{-5}
30.0	0.386	1.930	1.0×10^{-4}	2.3×10^{-5}	7.7×10^{-5}
30.0	0.456	2.373	1.0×10^{-4}	1.9×10^{-5}	8.1×10^{-5}
30.0	0.295	1.599	8.1×10^{-5}	2.0×10^{-5}	6.1×10^{-5}
35.0	0.297	1.069	1.1×10^{-4}	3.5×10^{-5}	7.5×10^{-5}
35.0	0.334	1.249	1.2×10^{-4}	3.7×10^{-5}	8.3×10^{-5}
35.0	0.376	1.487	1.1×10^{-4}	3.2×10^{-5}	7.8×10^{-5}
45.5	0.183	0.880	2.2×10^{-4}	7.1×10^{-5}	1.5×10^{-4}
45.5	0.193	0.609	2.2×10^{-4}	7.0×10^{-5}	1.5×10^{-4}
45.5	0.148	0.816	2.4×10^{-4}	8.2×10^{-5}	1.6×10^{-4}
			E_a, kcal/mol	17	13

TABLE II

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF 2-(α-BROMOBENZYL)-1,4-DIHYDRO-4,4-DIMETHYL-1-KETONAPHTHALENE (1a) WITH *tert*-BUTYLAMINE IN CHLOROFORM

Temp, °C	[Bromo ketone], mol/l.	[*tert*-Butylamine], mol/l.	k, l. mol^{-1} min^{-1}	k_1, l. mol^{-1} min^{-1}	k_2, l. mol^{-1} min^{-1}
15.0	0.162	0.924	6.1×10^{-5}	4.1×10^{-5}	2.0×10^{-5}
15.0	0.0837	0.0965	7.1×10^{-5}	5.1×10^{-5}	2.0×10^{-5}
15.0	0.181	1.654	7.2×10^{-5}	4.2×10^{-5}	3.0×10^{-5}
25.0	0.369	1.604	2.0×10^{-4}	1.3×10^{-4}	7.1×10^{-6}
25.0	0.369	2.406	2.6×10^{-4}	1.5×10^{-4}	1.1×10^{-4}
25.0	0.407	2.406	2.5×10^{-4}	1.4×10^{-4}	1.1×10^{-4}
30.0	0.358	0.855	2.7×10^{-4}	1.2×10^{-4}	9.4×10^{-5}
30.0	0.508	1.079	2.8×10^{-4}	1.8×10^{-4}	9.8×10^{-5}
30.0	0.265	1.238	2.4×10^{-4}	1.5×10^{-4}	8.6×10^{-5}
35.0	0.230	1.234	3.6×10^{-4}	2.3×10^{-4}	1.2×10^{-4}
35.0	0.350	1.443	3.7×10^{-4}	2.5×10^{-4}	1.2×10^{-4}
35.0	0.441	1.802	4.2×10^{-4}	2.7×10^{-4}	1.5×10^{-4}
45.5	0.137	0.594	8.2×10^{-4}	6.6×10^{-4}	1.6×10^{-4}
45.5	0.143	0.904	7.6×10^{-4}	5.8×10^{-4}	1.8×10^{-4}
			E_a, kcal/mol	15	12

TABLE III

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF 2-(α-BROMOBENZYL)-1,4-DIHYDRO-4,4-DIMETHYL-1-KETONAPHTHALENE (1a) WITH *tert*-BUTYLAMINE IN ACETONITRILE

Temp, °C	[Bromo ketone], mol/l.	[*tert*-Butylamine], mol/l.	k, l. mol^{-1} min^{-1}	k_1, l. mol^{-1} min^{-1}	k_2, l. mol^{-1} min^{-1}
15.0	0.157	0.642	9.9×10^{-4}	7.4×10^{-4}	2.5×10^{-4}
15.0	0.159	0.812	9.5×10^{-4}	7.1×10^{-4}	2.4×10^{-4}
30.0	0.154	0.690	3.4×10^{-3}	2.5×10^{-3}	8.5×10^{-4}
30.0	0.110	0.638	2.6×10^{-3}	2.0×10^{-3}	6.2×10^{-4}
30.0	0.156	0.647	3.7×10^{-3}	2.8×10^{-3}	8.9×10^{-4}
35.0	0.156	0.607	5.9×10^{-3}	4.7×10^{-3}	1.2×10^{-3}
45.5	0.148	0.580	1.3×10^{-2}	1.1×10^{-2}	2.2×10^{-3}
45.5	0.149	0.740	1.2×10^{-2}	9.7×10^{-3}	2.4×10^{-3}
			E_a, kcal/mol	16	13

Results and Discussion

The kinetics were found to be overall second order, first order in halo ketone **1** and first order in amine. The data best fits an equation involving two equivalents of amine, which is consistent with the overall scheme shown below. The second molecule of amine

$$R'X + RNH_2 \longrightarrow \overset{+}{R}NH_2R'X^- \xrightarrow{RNH_2} RNHR' + \overset{+}{R}NH_3X^-$$

acts as a base to free the amino ketone from its hydrobromide salt.

The activation energy for the reaction yielding direct substitution product was found to be 15–17 kcal/mol, while that for the rearrangement–substitution reaction was found to be 12–13 kcal/mol (Tables I–IV). The lower activation energy for the rearrangement–substitution reaction is consistent with the results of the study of the steric requirements of the reaction.[1] The carbonyl group is probably responsible for the lowering of the activation energy of the rearrangement reaction, relative to direct displacement. The carbonyl group can be expected to lower the activation energy of the abnormal substitution reaction in two ways. First, it can reduce the electron density at the γ carbon atom by the normal ground-state resonance effect. Secondly, it can act as an electron sink during the transition state to help disperse the developing charge.

Leaving Group Effect.—In Table V are listed the average rate constants obtained for the reaction of *tert*-butylamine with bromo ketone **1a** and chloro

TABLE IV

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF 2-(α-CHLOROBENZYL)-1,4-DIHYDRO-4,4-DIMETHYL-1-KETONAPHTHALENE (1b) WITH *tert*-BUTYLAMINE IN ACETONITRILE

Temp, °C	[Chloro ketone], mol/l.	[*tert*-Butylamine], mol/l.	k, l. mol^{-1} min^{-1}	k_1, l. mol^{-1} min^{-1}	k_2, l. mol^{-1} min^{-1}
30.0	0.152	0.582	1.7×10^{-4}	2.3×10^{-5}	1.5×10^{-4}
30.0	0.198	0.660	1.8×10^{-4}	2.3×10^{-5}	1.6×10^{-4}

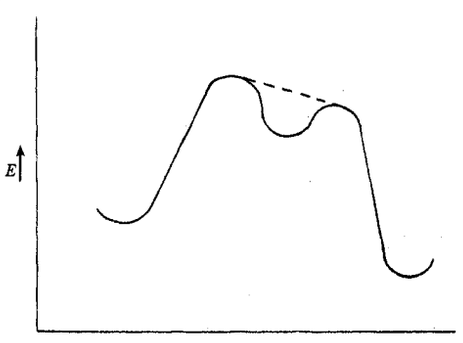
TABLE V

LEAVING GROUP EFFECT IN ACETONITRILE

Halo ketone	k, l. mol^{-1} min^{-1}	k_1, l. mol^{-1} min^{-1}	k_2, l. mol^{-1} min^{-1}	Relative rates k_1	Relative rates k_2
1a	3.2×10^{-3}	2.4×10^{-3}	8.2×10^{-4}	110	5.5
1b	1.8×10^{-4}	2.3×10^{-5}	1.5×10^{-4}	1	1

ketone **1b** at 30° in acetonitrile. It can be seen from the table that the bromo ketone **1a** reacts 110 times faster than the chloro ketone **1b** to yield the direct substitution product, but reacts only 5.5 times faster to yield the rearranged substitution product. The large "element effect" in the reaction yielding direct substitution product is consistent with a concerted SN2 reaction in which bond breaking has made significant progress in the rate-determining transition state. The smaller "element effect" for the reaction yielding rearrangement–substitution product is less easily interpreted.

If a stable dipolar intermediate were involved, and if addition of amine occurred in the rate-determining step, then a Br:Cl rate ratio of one would be predicted. That is, the carbon to halogen bond breaking occurs well after the rate-determining transition state, and an energy profile as in A, might best illustrate the reaction.



A

Small Br:Cl rate ratios have been observed in both aromatic nucleophilic substitution reactions ($k_{Br}/k_{Cl} \approx 1$–2)[4] as well as in nucleophilic vinyl substitution reactions ($k_{Br}/k_{Cl} \approx 2$–3).[5] In both cases the small leaving group effect has been cited in support of the addition–elimination mechanism. Bunnett and coworkers[6] have concluded that, while the small "element effect" in aromatic substitution reactions supports the presence of an intermediate and indicates that the breaking of the C–X bond has not made significant progress in the rate-determining transition state, it does not rule out the possibility of a synchronous reaction represented by the dotted line in the energy profile shown above. Thus a small Br:Cl rate ratio is in itself not rigorous evidence for an intermediate.

It should be recognized that the leaving group effect is probably solvent dependent. Indeed, in the reaction of *p*-nitrobenzene halides with piperidine the Br:Cl rate ratio varies from 1.16 in acetonitrile to 1.69 in benzene.[7] This is to be expected, since the more polar solvent would stabilize the dipolar intermediate more, leading to a smaller leaving group effect. Bordwell[8] has also observed a variation in leaving group effect with solvent. He has interpreted this to indicate that in the nonpolar solvent benzene ($k_{Br}/k_{Cl} = 16$) there is a dipolar transition state involved, but in the polar solvent ethanol ($k_{Br}/k_{Cl} = 1.4$) there is a dipolar intermediate involved.

The leaving group effect observed in this study is too large to support postulating an intermediate and, while small, it is significant, especially in as polar a solvent as acetonitrile. The leaving group effect is best interpreted as indicating that carbon–halogen bond breaking occurs late in the transition state. Another way of putting this is to say that the transition state of the reaction yielding abnormal substitution products is "reactantlike."

Solvent Effects.—Table VI contains a summary of the rate constants for the reaction of bromo ketone **1a** with *tert*-butylamine at 30° in the solvents benzene, chloroform, and acetonitrile. In the reaction yielding direct substitution product the rate enhancement in going from benzene to acetonitrile is 124. This is in accord with predictions based upon principles set forth by Ingold.[9] The more polar solvent stabilizes the charged transition state of the SN2 reaction involving neutral reactants, thereby substantially increasing the rate. By way of comparison, the relative rates of the reaction of trimethylamine with *p*-nitrobenzyl chloride in benzene, chloroform, and acetonitrile are 1:10.7:170.[10,11] It was concluded[11] that the charge separation in the transition state was small, although the degree of charge separation may vary from solvent to solvent.

TABLE VI

SOLVENT EFFECT ON THE RATE OF REACTION OF *tert*-BUTYLAMINE WITH BROMO KETONE 1b

Solvent	k_1, l. mol^{-1} min^{-1}	Relative rate	k_2, l. mol^{-1} min^{-1}	Relative rate
C_6H_6	2.1×10^{-5}	1	7.3×10^{-5}	1
$CHCl_3$	1.5×10^{-4}	7.1	9.3×10^{-5}	1.3
CH_3CN	2.6×10^{-3}	124	7.9×10^{-4}	11

The relative rates for the reaction yielding abnormal

(4) (a) J. Miller, "Aromatic Nucleophilic Substitution," Elsevier, New York, N. Y., 1968, p 114; (b) J. F. Bunnett in "Theoretical Organic Chemistry," Kekule Symposium, Butterworths, London, 1959, p 144.

(5) (a) Z. Rappoport, *Advan. Phys. Org. Chem.*, **7**, 1 (1971); (b) G. Modena, *Accounts Chem. Res.*, **4**, 73 (1971); (c) A. Campagni, G. Modena, and P. E. Todeseo, *Gazz. Chim. Ital.*, **90**, 694 (1960).

(6) J. F. Bunnett, E. W. Garbisch, Jr., and K. M. Pruitt, *J. Amer. Chem. Soc.*, **79**, 385 (1957).

(7) H. Suhr, *Chem. Ber.*, **97**, 3277 (1964).

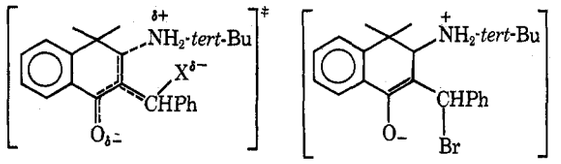
(8) F. G. Bordwell and D. A. Schexnayder, *J. Org. Chem.*, **33**, 3236 (1968).

(9) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, p 457.

(10) H. v. Halban, *Z. Phys. Chem.*, **84**, 129 (1913).

(11) (a) M. H. Abraham, *Chem. Commun.*, 1307 (1969); (b) M. H. Abraham, *J. Chem. Soc. B*, 299 (1971).

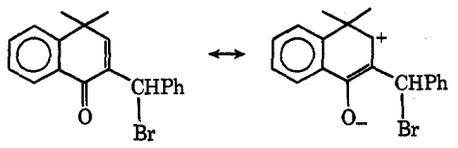
substitution product in benzene, chloroform, and acetonitrile are 1:1.3:11. This reaction also involves neutral reactants going to a charged transition state as in the classical Menschutkin reaction and should, therefore, be very sensitive to solvent polarity. One possible explanation for the small solvent effect observed in this reaction is that the developing charge is dispersed over several nuclei. It is not unreasonable to assume that some of the developing charge is located on the carbonyl group, as well as on the halogen ion, which has been shown by the leaving group effect to be involved in the transition state. A "picture" of the transition state emerges from this discussion and may be postulated as in B. The intermediate B has fully



A B

developed charges which would be expected to be stabilized by the more polar solvent, perhaps to a greater degree than is observed. Nucleophilic aromatic substitution reactions in which a dipolar intermediate is postulated exhibit solvent effects of the order $k_{CH_3CN}/k_{C_6H_6}$ = 24–35,[7] while addition of amines to α,β-unsaturated carbonyl compounds which may also involve dipolar intermediates exhibit small solvent effects.[12] Thus, while the solvent effect observed does not rigorously rule out a dipolar intermediate such as B, a charge dispersed transition state, as in A, accommodates all the data.

Proposed Mechanism.—The halo ketones **1** may react by direct displacement at the 2α position or by rearrangement–substitution *via* attack at the 3 position. Although the 3 position would appear to be sterically hindered by the geminal methyl groups on the 4 carbon, attack takes place at the 3 position to the exclusion of direct displacement with small amines.[1] The lower activation energy of the rearrangement–substitution reaction is probably brought about by the carbonyl group, which reduces the electron density at the 3 position by the normal resonance effect in the ground state of the molecule as shown below. With more space-demanding amines, such as *tert*-butylamine, the rearrangement–substitution reaction is made sterically more difficult, and the direct displacement at the 2-α position becomes competitive with rearrangement–



substitution.[1] The rearrangement–substitution reaction, however, is still a lower energy process than direct displacement. These first formed products, being thermodynamically less stable than the normal substitution products, then may react with a second molecule of amine to yield the final thermodynamically stable isomers.[1] It is likely that this second aminotropic rearrangement–substitution occurs with a cis configuration of entering and leaving amine, since this reaction is quite sensitive to the steric requirements of the amines.

Bromo ketone **1a** reacts with *tert*-butylamine by two parallel paths: direct SN2 displacement of halide to yield amino ketone **2** and an SN2′-type displacement to yield amino ketone **3**. The direct displacement reaction is characterized by a large leaving group effect k_{Br}/k_{Cl} = 110, as well as by a large solvent effect $k_{CH_3CN}/k_{C_6H_6}$ = 124, both fairly typical of Menschutkin-type reactions.

The rearrangement–substitution reaction does not appear to proceed *via* Michael 1,4 addition of amine to the s-trans enone system. Thus, an SN2′-type reaction is most likely. The relatively small solvent effect ($k_{CH_3CN}/k_{C_6H_6}$ = 11) and the small leaving group effect (k_{Br}/k_{Cl} = 5.5), while not ruling out the possibility of a dipolar intermediate, argue against such an intermediate.

Therefore, with no strong evidence to support an intermediate, we feel that all the data is best interpreted in the following manner. In a concerted process, the amine attacks the 3 position which is polarized by resonance with the carbonyl. Before the complete development of the negative charge on the carbonyl oxygen, the carbon–halogen bond begins to break. Thus, this mechanism may best be considered to be a variant of an SN2′-type reaction in which the entering of the amino group and the departure of the halogen ion are concerted, but the carbon to nitrogen bond making is running ahead of carbon to halogen bond breaking, and the carbonyl group serves to disperse some of the developing negative charge.

Experimental Section[13]

Preparation of Materials. Halo Ketones.—All halo ketones were prepared by the previously published procedure[2] and the physical data compared favorably with published values. The halo ketones were recrystallized from CCl_4 or isopropyl ether twice, powdered in a mortar and pestle, and dried in a desiccator. Nmr and tlc showed the halo ketones to be pure.

***tert*-Butylamine.**—Commercially available *tert*-butylamine, of reagent grade or better, was dried over BaO and distilled twice using a Vigreux column. The constant-boiling fraction was stored in a glass-stoppered flask covered with aluminum foil to exclude light.

Solvents.—Reagent grade solvents were used in all cases. The benzene was dried over sodium, acetonitrile was dried over P_2O_5, and the chloroform was passed through a column of alumina (Woelm activity I) to remove water and ethanol. After drying, the solvents were distilled using a Vigreux column and stored in a glass-stoppered flask. The chloroform was used within a week to prevent interference from phosgene.

General Procedure.—The dry halo ketone was weighed by difference into a volumetric flask (25, 50, or 100 ml) with the aid of a small funnel. The halo ketone was then dissolved in the appropriate solvent and the funnel was washed well with solvent. The amine was then weighed by addition into a glass-stoppered weighing bottle. After an initial rough weighing, the stopper was replaced, a fine weighing was made, and the flask was placed in an ice bath. The amine was then added to the solution of the halo ketone with a pipet, the weighing bottle was rinsed several

(12) (a) K. L. Mallik and M. N. Das, *Z. Phys. Chem. (Frankfurt am Main)*, **25**, 205 (1960); (b) F. M. Menger and J. H. Smith, *J. Amer. Chem. Soc.*, **91**, 4211 (1969).

(13) All nmr spectra were obtained on a Varian A-60 or A-60D spectrometer. Eastman silica gel chromagram sheet 6060 with fluorescent indicator was used in a solvent system consisting of *n*-hexane, ethyl acetate, and benzene in a ratio of 1:1:8 for all tlc. Rate constants and activation energies were calculated on an IBM 360 computer by the least-squares method.

times with solvent, and the volume was made up (to 25, 50, or 100 ml) with additional solvent. After mixing well, the solvent was delivered by means of a pipet into test tubes having a constriction. The test tubes were placed in a Dry Ice–acetone bath and then sealed. The sealed tubes were then placed in a constant-temperature bath and removed at appropriate intervals for analysis. Because the reaction was slow, it was not found necessary to either cool the volumetric flask below room temperature when aliquots were being removed or to take an initial reading at time = 0 min. At appropriate intervals, a sealed tube was removed from the bath, opened, and filtered into a 50-ml flask. The tube was washed several times with solvent and these washings were added to the flask. The combined filtrate and washings were evaporated under vacuum without heating. The oily residue was dissolved in $CDCl_3$ (0.3 ml) and filtered into an nmr tube. This final filtering was necessary to remove the amine hydrobromide which was dissolved in the original solvent.

For each run 8–10 points were obtained for up to 80% completion. The ratio of **2** to **3** remained constant, within experimental error, over the course of the reaction.

Analysis.—The general appearance of the spectrum was observed at a sweep width of 500 Hz, scanning from approximately 400 to 200 Hz. This was necessary so that spinning side bands, which might be near the methine absorption of the halo ketone, could be shifted away be varying the sample spin rate. The methine absorptions of the halo ketone and both amino ketones were recorded at a sweep width of 50 Hz and at a sweep time of 250 or 500 sec. Saturation of absorbances did not occur during integration which was performed at a sweep time of 50 sec. Each of the absorbances was electronically integrated 8 to 12 times, depending upon reproducibility.

The assumption was made that the sum of the concentrations of halo ketone and both amino ketones was a constant and was equal to the initial concentration of halo ketone. In this way, a quantitative internal standard was unnecessary. Furthermore, the actual size of the aliquot taken and the volume to which the sample was made up were not important. The overall rate constants were calculated assuming that 2 equiv of amine are consumed. The following equation was used in these calculations where a_0 = initial concentration of amine, b_0 = initial concentration of halo ketone, and x = amount of reaction or concentration of both products.

$$\frac{1}{(a_0 - 2b_0)} \ln \frac{b_0(a_0 - 2x)}{a_0(b_0 - x)} = (k_1 + k_2)t$$

The individual rate constants k_1 and k_2 were then determined by multiplying the observed rate constant by the fraction of each product obtained.

Registry No.—**1a**, 33224-47-4; **1b**, 15982-14-6; *tert*-butylamine, 75-64-9.

Acknowledgments.—This work was supported in part by a Special Departmental Science Development Award to the Department of Chemistry from the National Science Foundation, No GU-2054, and in part by a grant from the Nebraska Research Council. One of us (G. G.) wishes to acknowledge financial assistance received in the form of an NSF traineeship and a Monsanto summer fellowship. The authors also wish to thank Mr. Russ Pennelly for the computer programs.

Secondary Valence Force Catalysis. XIII. Kinetics of the Alkaline Fading of Crystal Violet in the Presence of Cationic Surfactants[1]

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Received July 26, 1971

The alkaline fading of crystal violet in aqueous solution at 30° is subject to catalysis by dilute solutions of *n*-alkyltrimethylammonium bromides. Catalytic effectiveness of these surfactants increases markedly with increasing alkyl chain length as judged both by the maximal rate increase elicited and by the surfactant concentration required to elicit the maximum catalysis. The best catalyst studied, octadecyltrimethylammonium bromide, increases the rate constant for the fading reaction 30-fold at a concentration of 0.0003 *M*. The surfactant-dependent reactions are subject to marked inhibition by anions and by the nonionic surfactant dodecyldimethyl phosphine oxide. The effectiveness of the anions as inhibitors increases in the order $F^- < Cl^- < Br^- < N_3^- < NO_3^-$.

During the last several years there have appeared a substantial number of publications dealing with the kinetics of organic reactions in the presence of micelle-forming surfactants. These studies have been recently reviewed.[2,3] Among them, one of the more notable investigations is that of Duynstee and Grunwald concerning the kinetics of fading of triphenylmethyl dyes.[4] These workers observed catalysis of the attack of hydroxide ion on these cationic dyes by cationic surfactants and marked inhibition for the same reaction by anionic surfactants. The attack of water on these dyes was found subject to inhibition by both cationic and anionic dyes. In many respects, this seminal study provided the basis for later ones concerning other reactions. A subsequent study by Ritchie and coworkers, employing surfactant-free media, has extended study of the uncatalyzed reaction to include additional nucleophiles and has clarified some mechanistic details, including the possible importance of solvent reorientation in the activation process for these reactions.[5] Both in light of this new work and in view of gaps in our information concerning the kinetics of the surfactant-catalyzed reactions, additional study seems warranted. Specifically, there is no available information concerning the effects of surfactant concentration, of surfactant structure, or of salts on the reaction kinetics. To provide this information, we have examined the kinetics of attack of hydroxide ion on crystal violet [tris(*p*-dimethylaminophenyl)methyl cation] in the presence of a series of *n*-alkyltrimethylammonium bromides.

(1) Publication No. 2021 from the Department of Chemistry, Indiana University. Supported by the Escuela de Quimica, Universidad Central and by Grant AM 08232 from the National Institutes of Health. E. H. Cordes (Indiana University) supported by a Career Development award from the National Institutes of Health, Grant K03 GM10248.

(2) E. J. Fendler and J. H. Fendler, *Advan. Phys. Org. Chem.*, **8**, 271 (1970).

(3) E. H. Cordes and R. B. Dunlap, *Accounts Chem. Res.*, **2**, 329 (1969).

(4) E. F. J. Duynstee and E. Grunwald, *J. Amer. Chem. Soc.*, **81**, 4540, 4542 (1959).

(5) C. D. Ritchie, G. A. Skinner, and V. G. Badding, *ibid.*, **89**, 2063 (1967).