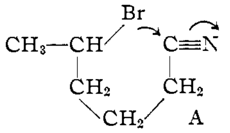
by Winstein and co-workers[12]; it was found to be 2.37 kcal./mole.

It is rather strange that acetoxy and bromo groups at the δ-position were found to have no significant effect upon the rates, when one recalls that the neighboring group effects of those groups at the β-position are quite large,[12] especially in the case of a bromo group which is fairly nucleophilic in nature.

It is also interesting that the cyano group retards the reaction. In this case, since the cyano group is highly electron-withdrawing, there would be a fairly large electrostatic attraction between the nucleophilic bromo group and the carbon atom of the cyano group, as shown in (A); and in order for the bromide to formolyze, it would be necessary to break this attraction, which would require a small amount of energy and in turn would result in the retardation of the reactivity. Another possible explanation is based upon a purely inductive mechanism. Since the cyano group is highly electron withdrawing, the simple inductive effect could have caused the retardation of SN1 reactivity of the bromide, while the bromo group in 2,5-dibromopentane, although quite strongly electron withdrawing, might have canceled out its effect by its nucleophilic participation from the back side at the transition state, which would hardly be possible in the case of cyano group. However, the latter explanation seems to be less probable, because the inductive effect is not usually transmitted through more than three saturated methylene linkages.[3,13]



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Acknowledgment.—The author is most grateful to Professor M. Murakami who encouraged him all through this study. He wishes to express his sincere appreciation to Professor Charles C. Price for his helpful suggestions.

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[12] S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 928 (1948).

[13] See succeeding paper, Paper V of this series, *ibid.*, **78**, 4034 (1956).

OSAKA, JAPAN

[CONTRIBUTION FROM THE INSTITUTE OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OSAKA UNIVERSITY]

Effect of Substituent on the Reactivity of ω-Substituted Primary Alkyl Halide in the Reaction with Sodium Thiosulfate[1,2]

BY KATSUHIKO AKAGI, SHIGERU OAE[3,4] AND MASUO MURAKAMI

RECEIVED FEBRUARY 20, 1956

Rate constants, heat of activation and entropies of activation have been determined for several series of ω-substituted primary alkyl halides in their reaction with sodium thiosulfate in 50% ethanol. No alternation effects were observed in most of the series. In all series examined, electron-withdrawing substituents were found to increase the value of the heat of activation.

Since the well-known work of Conant and his co-workers,[5] the phenomenon of alternating reactivities has been re-observed or re-interpreted by many other workers[6] from time to time. Among all, Dewar's interpretation by means of hyperconjugation seemed to be elegant and in fact the decomposition rates of ω-nitrosoacetaminoalkylbenzenes were very well explained by his theory.[7] However, the particular phenomenon was not observed in the SN1 type reactivities of ω-substituted primary alkyl halides in the reaction with mercuric nitrate.[8] Therefore, the alternation of reactivities in the reaction with potassium iodide in acetone, which was referred to by Dewar for his interpretation of the alternation effect, does not seem to originate from pure electrical effect, such as the "alternating polarity," as far as this particular reaction is concerned.

Meanwhile, there is a possibility that the steric effect is responsible for the alternation of reaction rates. As is known in the case of ethylene dihalides the *trans* form is considered to be the most stable form at the normal state.[9] But the *trans* form is sterically handicapped for SN2 reaction and therefore would isomerize to the *gauche* or *cis*-form in the transition state. This process would consume a small amount of energy. If the energies required in this process are varied alternatively according to the number of the chain, it would affect the activation energy and in turn would cause the alternation of reaction rates. However, this assumption was found to be implausible. We have chosen *cis*- and *trans*-dichloropropenes as the similar models. Fisher–Hirschfelder models of these compounds clearly show that the *trans* form is sterically more favorable than the *cis* form in the SN2 reaction. And yet there was found no practical difference in the values of their heats of activa-

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[1] Paper V on "Reactivities of Organic Halides in Displacement Reactions"; Paper IV, THIS JOURNAL, **78**, 4032 (1956).

[2] Presented at the 8th General Meeting of the Japanese Chemical Society, Tokyo, April, 1955.

[3] John Harrison Laboratory of Chemistry, University of Pennsylvania, Philadelphia 4, Pa.

[4] To whom requests for reprints should be addressed.

[5] J. B. Conant and W. R. Kirner, THIS JOURNAL, **46**, 232 (1924); J. B. Conant, W. R. Kirner and R. B. Hussey, *ibid.*, **47**, 488 (1925).

[6] E. Müller, "Neuere Anschaungen der organischen Chemie," Julius Springer, Berlin, 1940, pp. 66–73; M. J. B. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, 1949, pp. 157–159.

[7] M. Murakami and K. Akagi, *J. Chem. Soc., Japan*, **75**, 532 (1954).

[8] (a) S. Oae and C. A. VanderWerf, THIS JOURNAL, **75**, 5037 (1953); (b) S. Oae, *ibid.*, **78**, 4030 (1956).

[9] L. N. Ferguson, "Electron Structures of Organic Molecules," Prentice Hall Book Co., New York, N. Y., 1952, pp. 93–100.

tion in the reaction with thiosulfate ion, as shown in Table I.

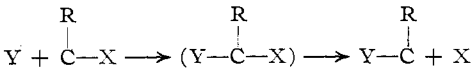
TABLE I

RATE CONSTANTS FOR THE REACTION OF *cis*- AND *trans*-1,3-DICHLOROPROPANE WITH SODIUM THIOSULFATE IN 50% ETHANOL

Dichloro-propene	Temp., °C.	$k \times 10^3$, mole^{-1} l.	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e.u.
trans-1,3-	12.2	1.60 ± 0.08		
	24.6	4.84 ± .05		
	37.4	13.7 ± .1	14.5	−18.3
cis-1,3-	12.2	2.59 ± .03		
	24.6	7.42 ± .07		
	37.4	21.6 ± .5	14.4	−17.7

Another consideration is based upon the entropy change. Ingold has suggested[10] that the increase of non-bonding energy due to the addition of a methylene group is responsible for the decrease of rate from ethyl to propyl in an SN2 reaction. Namely, the freedom of rotation is lowered by the longer substituents. In this case, the rate would be affected by the change in $\Delta S^{\ddagger}$. This interpretation is very well applied to the unsubstituted normal chain alkyl halides and was also found to be applicable to our case, as seen in Table II. However, the entropy change is the decisive factor only in cases where the polar effect is equal or is canceled out. In most reactions of polar group substituted alkyl halides, polar effect seems to be predominant. Although fragmentary ideas can be obtained through many previous works,[11] there have not been many reports which cover wide varieties of both unsubstituted and ω-substituted normal alkyl halides, nor are there many reactions in which accurate measurements are possible to calculate both heat and entropy of activation. Among these reactions, the one with sodium thiosulfate seemed to be most promising.[11f] Accordingly, this reaction was used in this investigation.

Now, let us set aside the steric effect and consider the electrical effect in an SN2 reaction. Unlike the SN1 mechanism, polar requirements are not clear-cut in the bimolecular mechanism. SN2 reactions are single stage processes, in which the bond fission of C–X occurs simultaneously with the bond formation of Y–C as in the equation



$$\mathrm{Y} + \overset{\overset{\mathrm{R}}{|}}{\mathrm{C}}\text{—X} \longrightarrow (\mathrm{Y}\text{—}\overset{\overset{\mathrm{R}}{|}}{\mathrm{C}}\text{—X}) \longrightarrow \mathrm{Y}\text{—}\overset{\overset{\mathrm{R}}{|}}{\mathrm{C}} + \mathrm{X}$$

in which bond fission should be facilitated if R is of electron-releasing nature, while the approach of the nucleophilic reagent should be hindered and *vice versa*. Many previous workers or reviewers[12] have referred only to such reactions in which bond forming requirements appeared to be dominant and so it has been commonly thought that an electron-withdrawing R facilitated the reaction while an electron-releasing R retards it. But the references cited are not completely adequate and in many reactions only velocity constants are available. Only recently there have appeared a few systematic studies.[11f,g] Especially, the work of Hine and Brader[11g] on the reactions of β-substituted ethyl bromides with thiophenolate ion has shown that electron-withdrawing substituents reduce the rate of reaction, which in turn indicates the domination of the bond fission stage in this SN2 reaction. Our results on the reaction of ω-substituted normal chain alkyl bromides with sodium thiosulfate are presented in Table II.

Here again, electron-withdrawing substituents such as ethoxy, chloro and ethylsulfonyl groups were found to retard the reaction. The heat of activation increases successively with the successive approach of the ω-substituted electron-withdrawing group to the α-carbon; thus bond fission requirements are dominant in the reaction between these ω-substituted alkyl bromides and sodium thiosulfate. As Ingold[10] and later Hine, *et al.*,[11g] have already pointed out, the successive decrease in reactivity from ethyl to propyl is well attributed to the restriction of free rotation around the Cα–Cβ bond in the transition state, and the rate change is affected only by the entropy change. The successive decrease of the entropy term according to the increase of chain length was also observed in all series, except in the series of ω-phenyl-substituted alkyl bromides, where alternation of entropy values was observed and was found to be responsible for the alternation of the rates. As can be seen from the series of simple unsubstituted alkyl bromides[13] and those of ω-phenyl-substituted alkyl bromide, the alkyl or the phenyl group has little polar nature, and in the reaction of such compounds, the entropy change is the decisive factor in the rate change; however, when these compounds are substituted by some polar group, its inductive effect exerts a strong influence upon the heat of activation, which usually becomes the dominant factor for the rate change. Our results, as well as those of Hine and Brader, on β-substituted ethyl bromides[11g] and also the recent findings on α-substituted halides by Hine, *et al.*,[14] clearly indicate that all electron-withdrawing sub-

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(10) N. Ivanoff and M. Magat, *J. Chem. Phys.*, **47**, 914 (1950); E. Bauer and M. Magat, *ibid.*, 922 (1950)—see C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 410-411.

(11) (a) H. M. McKay, THIS JOURNAL, **65**, 702 (1943); (b) P. D. Bartlett and L. J. Rosen, *ibid.*, **64**, 643 (1942); (c) M. L. Dhar, E. D. Hughes, C. K. Ingold and S. Masterman, *J. Chem. Soc.*, 2055 (1948); (d) H. Seeling and D. E. Hull, THIS JOURNAL, **64**, 940 (1942); (e) S. Sugden, *et al.*, *J. Chem. Soc.*, 1279, 1836 (1939); 586 (1945); (f) T. I. Crowell and L. P. Hammett, THIS JOURNAL, **70**, 3444 (1948), P. M. Dunbar and L. P. Hammett, *ibid.*, **72**, 109 (1950); (g) J. Hine and W. H. Brader, Jr., THIS JOURNAL, **75**, 3964 (1953); (h) S. C. J. Olivier, *Rec. trav. chim.*, **56**, 247 (1937); (i) M. S. Newmau, THIS JOURNAL, **72**, 4753 (1950); (j) T. I. Crowell, *ibid.*, **75**, 6046 (1953).

(12) (a) V. V. Tronov and A. T. Gersevic, *J. Russ. Phys. Chem. Soc.*, **59**, 727 (1927); see A. E. Remick in "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 394, and M. J. S. Dewar in "The Electronic Theory of Organic Chemistry," Oxford University Press, New York, N. Y., 1949, p. 71: (b) G. Braddely and G. M. Bennett, *J. Chem. Soc.*, 1819 (1935); 261 (1933); (c) P. D. Bartlett, *The Study of Organic Reaction Mechanisms* in Gilman's "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 25-35.

(13) The observed kinetic values of ethyl and of *n*-propyl bromide are quite different from those of Crowell and Hammett.[11f] The differences might have come from the different compositions of the solvents. The larger reactivities in our case would be attributed to the less polar nature of the solution which has been suggested to decrease the heat of activation (see E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 252 (1935)).

(14) J. Hine, C. H. Thomas and S. J. Ehrenson, THIS JOURNAL, **77**, 3886 (1955).

TABLE II

RATES CONSTANTS FOR THE REACTION OF ω-SUBSTITUTED ALKYL BROMIDES WITH SODIUM THIOSULFATE IN 50% ETHANOL

Compound	Temp., °C.	$k \times 10^3$ (mole^{-1}, sec.$^{-1}$, l.)	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e.u.
Ethyl bromide	12.3	0.298 ± 0.003		
	24.9	1.07 ± .01		
	37.3	3.33 ± .03	16.2	−15.7
n-Propyl bromide	12.3	0.175 ± .001		
	24.9	0.631 ± .004		
	37.3	1.94 ± .02	16.2	−16.9
n-Butyl bromide	12.3	0.132 ± .001		
	24.9	0.465 ± .003		
	37.3	1.47 ± .01	16.1	−17.5
β-Bromoethyl ethyl ether	37.3	0.344 ± .002	18.3	−13.7
	49.8	1.16 ± .02		
	62.5	3.44 ± .02		
γ-Bromopropyl ethyl ether	24.9	0.407 ± .003		
	37.3	1.36 ± .01	17.0	−15.0
	49.8	4.04 ± .02		
δ-Bromobutyl ethyl ether	24.9	0.726 ± .007		
	37.3	2.35 ± .02	16.5	−15.6
	49.8	6.74 ± .06		
β-Chloroethyl bromide	24.9	0.107 ± .002		
	37.3	0.376 ± .003	18.3	−13.5
	49.8	1.26 ± .01		
γ-Chloropropyl bromide	24.9	0.405 ± .002		
	37.3	1.35 ± .01	17.4	−13.6
	49.8	4.26 ± .01		
δ-Chlorobutyl bromide	12.3	0.197 ± .002		
	24.9	0.734 ± .002		
	37.3	2.33 ± .01	16.6	−15.0
β-Bromoethyl ethyl sulfone	24.9	0.722 ± .011		
	37.3	2.60 ± .05	19.2	− 9.2
	49.8	8.08 ± .18		
γ-Bromopropyl ethyl sulfone	24.9	3.58 ± .11		
	37.3	12.3 ± .3	17.2	−12.3
	49.8	33.3 ± .1		
(β-Bromoethyl)-benzene	37.3	0.890 ± .006		
	49.8	3.24 ± .03	17.9	−13.0
	62.5	8.47 ± .01		
(γ-Bromopropyl)-benzene	24.9	0.417 ± .002		
	37.3	1.53 ± .02		
	49.8	4.65 ± .03	17.9	−12.0
(δ-Bromobutyl)-benzene	37.3	1.36 ± .02		
	49.8	4.34 ± .02	17.8	−12.4
	62.5	12.8 ± .1		

stituents increase the heat of activation, that is, tend to decrease the rate in S_N2 reactions, with possibly one exception, *i.e.*, the α-substituted carbonyl group, in which the reaction mechanism has been considered to be slightly different.[15] The different trends of entropy change from simple alkyl bromides to phenyl-substituted alkyl bromides cannot be explained by our present knowledge.

There is one more exception which seemingly does not fit in the above category. In allylic chlorides, electron-withdrawing groups such as chloro, sulfonyl and cyano increase the rate.[16] But the rates have been measured at only one temperature and detailed calculations of both heats of activation as well as entropies of activation are lacking. Our results on these γ-substituted allylic chlorides in the reaction with thiosulfate ion have indicated, as seen in Table III, that the electron-withdrawing group increased the rate but that the rate increase is not affected by the heat of activation, but by the entropy change. Heats of activation are found again to be larger in the cases of allylic chlorides substituted by electron-withdrawing groups. Here again the bond fission stage seems to be dominant in this bimolecular mechanism.

TABLE III

RATE CONSTANTS FOR THE REACTION OF γ-SUBSTITUTED ALLYLIC CHLORIDES WITH SODIUM THIOSULFATE IN 50% ETHANOL

Compound	Temp., °C.	$k \times 10^3$, mole^{-1}, sec.$^{-1}$, l.	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e.u.
Allyl chloride	12.2	0.932 ± 0.01		
	24.6	2.51 ± .04		
	37.4	7.33 ± .03	13.8	−21.7
trans-1,3-Dichloropropene	12.2	1.60 ± .08		
	24.6	4.94 ± .05		
	37.4	13.7 ± .1	14.5	−18.3
cis-1,3-Dichloropropene	12.2	2.59 ± .03		
	24.6	7.42 ± .07		
	37.4	21.6 ± .5	14.4	−17.7
Chloromethylvinyl ethyl sulfone	12.3	1.71 ± 0.07		
	24.9	5.36 ± .21		
	37.3	18.0 ± .6	15.8	−13.7

Acknowledgment.—We would like to express our sincere thanks to the Ministry of Education for the Grant as well as the Grant-in-Aid for the Scientific Research and particularly to the Society of Sigma Xi for the Grant-in-Aid which enabled us to buy the necessary chemicals from the United States. We would also like to express our deep gratitude to Mr. Takuzo Fujino who kindly offered his effort to calibrate all the volumetric apparatus. We are also grateful to Professor Charles C. Price who kindly read this manuscript.

Experimental

Materials.—Commercial absolute ethanol was refluxed over calcium oxide for several hours and then distilled through an efficient column and the fraction distilled at 78.0° (759 mm.) was collected.

The solvent, "50% ethanol," was made by diluting 500 ml. of absolute ethanol with distilled water to 1 l. at 20°; d^{25}_{4} was 0.9245, which corresponds to 44.6% of ethanol by weight.

Commercially available analytical grade sodium thiosulfate and sodium acetate were used without further purification.

Commercially available iodine was purified by repeated sublimation.

A mixture of *cis*- and *trans*-1,3-dichloropropene[17] was fractionated through an efficient column. The fractions distilling at 104 and 111° at 760 mm. were collected separately, washed with 10% sodium bicarbonate solution and dried over calcium chloride. Each well dried fraction was repeatedly fractionated through an efficient column. The lower boiling isomer, $n^{20}\text{D}$ 1.4687, has been assigned to the *cis*-configuration and the higher boiling isomer, $n^{20}\text{D}$ 1.4751, the *trans*-configuration.[18]

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(15) E. N. Trachtenberg, Thesis, Harvard University, 1952. See P. D. Bartlett, The Study of Organic Reaction Mechanisms, in Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 35.

(16) (a) F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **73**, 5184 (1951); (b) S. Oae, *Waseda Applied Chem. Bull.*, **21**, No. 1, 7 (1952). No. 2, 8 (1953).

(17) Obtained through the kindness of the Shell Development Co., Calif.

(18) L. F. Hatch and P. H. Perry, Jr., THIS JOURNAL, **71**, 3262 (1949).

Ethyl, *n*-propyl and *n*-butyl bromides were all prepared from the corresponding alcohols by treatment with a mixture of sodium bromide and sulfuric acid, and the bromides obtained were washed with concentrated sulfuric acid, water, 10% sodium carbonate solution, again with water, then dried over calcium chloride and finally fractionally distilled just before use.

Eastman Kodak C.P. β-bromoethyl ethyl ether was washed, dried and distilled and the fraction boiling at 125° (760 mm.) was collected.

Both γ-bromopropyl ethyl ether and α-bromobutyl ethyl ether were prepared and purified by the methods described elsewhere.[5b]

β-Chloroethyl bromide and γ-chloropropyl bromide were both Eastman Kodak white label products. Both were purified as in the case of alkyl bromides.

γ-Chlorobutyl bromide or 1-bromo-4-chlorobutane was prepared by the method used by the previous workers[19] and the fraction boiling at 103–104° (110 mm.) was collected.

Both β-bromoethylbenzene and γ-bromopropylbenzene were Eastman Kodak Co. white label products. δ-Bromobutylbenzene was prepared by the method described elsewhere.[8a] All these bromides were purified as in the previous work.[8a]

β-Bromoethyl ethyl sulfone was prepared by oxidizing β-bromoethyl ethyl sulfide with 30% hydrogen peroxide in acetic acid solution. The fraction boiling at 126–128° (3.5 mm.) was collected and used.

γ-Bromopropyl ethyl sulfone was also obtained by the same treatment starting from γ-bromopropyl ethyl sulfide (n^{20}_D 1.5113, b.p. 54–56° (5 mm.)), which was made by the reaction between a little excess trimethylene bromide and sodium ethylmercaptide in rather poor yield. The fraction of the oxidized compound boiling at 140° (4 mm.) was collected and used; yield 66%. This compound solidified at room temperature (around 15°).

Allyl chloride was Eastman Kodak Co. white label product, while the preparation of chlorovinyl ethyl sulfone is described elsewhere.[16b]

The Rate Determination.—The rate measurements were made according to those of Hammett and his co-workers.[11f] However, in our case, accurately measured initial concentrations were used for the calculations; in other words, the equation was used

$$k = \frac{2.03}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

The concentrations of sodium thiosulfate and organic halide were 0.1 *N*, while that of sodium acetate was maintained as 0.01 *N*, except in two series, *i.e.*, ω-phenylalkyl bromides and allylic chlorides. In both cases the concentrations of both sodium thiosulfate and organic halide were just half of those of the other experiments, while maintaining the concentration of sodium acetate as the same, since allylic chlorides were too reactive with the ordinary concentrations while ω-phenyl bromides were found not to be soluble in the ordinary concentration.

OSAKA, JAPAN

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[19] J. Cason, L. Wallcave and C. N. Whiteside, *J. Org. Chem.*, **14**, 37 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Interaction of Alkyl Halides with Dimethylformamide[1]

BY NATHAN KORNBLUM AND ROBERT K. BLACKWOOD[2]

RECEIVED OCTOBER 21, 1955

Solutions of alkyl halides in dimethylformamide undergo dehydrohalogenation and salt formation on standing at room temperature.

Alkyl halides react with dimethylformamide (DMF) at room temperature. This rather unexpected reaction, while not rapid, does occur at a significant rate (*cf.* Table I).[3,4]

These reactions were followed by titration of the acid formed or by titration of halide ion produced. Only in one case was an organic product isolated and characterized; from a DMF solution of *t*-butyl bromide, isobutylene was obtained in 46% yield.[5]

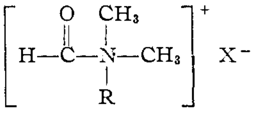
The kinetics of the reaction of three of the compounds listed in Table I were studied. The first-order rate constants ($k_1 \times 10^7$ sec.$^{-1}$) are: 1-iodobutane 3.39, 2-iodobutane 7.22, *t*-butyl bromide 24. These relative rates are in the order primary < secondary < tertiary and this, plus the fact that isobutylene is isolated, strongly suggests that dehydrohalogenation is an important factor. However, since DMF solutions of methyl iodide and benzyl bromide liberate halide ion, it is apparent that a second process, nucleophilic displacement, occurs, presumably to form the salt I.

TABLE I

INTERACTION OF ALKYL HALIDES WITH DMF

Halide	Concn., mole/liter	Temp., °C.	Reaction, (% complete)[a]
Methyl iodide	0.2	25–30	10%, 12 days
1-Iodobutane	.100	25	41%, 17 days
2-Iodobutane	.100	25	69%, 19 days
Benzyl bromide	.2	25–30	10%, 19 days
1-Bromoöctane	.200	25–30	64%, 324 days
2-Methyl-1-bromopropane	.200	25–30	25%, 280 days
2-Bromoöctane	.200	25–30	79%, 304 days
t-Butyl bromide	.100	25	75%, 7 days

[a] The reaction was followed only to the percentage completion given.

I 

$$\left[\mathrm{H{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\underset{\displaystyle R}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{N}}}}{-}CH_3}\right]^+ X^-$$

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[1] This research was supported by the United States Air Force under Contract No. AF 18 (600)-310 monitored by the Office of Scientific Research, Air Research and Development Command.

[2] E. I. du Pont de Nemours and Co. Fellow 1954–1955.

[3] It was first noted when the conductivity of a DMF solution of *n*-heptyl iodide was measured. A large increase in conductivity with time suggested the formation of ions [D. D. Mooberry, Ph.D. Thesis, Purdue University, 1954].

[4] A referee has kindly called our attention to a paper by G. M. Coppinger [THIS JOURNAL, **76**, 1372 (1954)] in which benzyl chloride is shown to react with DMF when heated at 150° for 6 hr. The two products isolated were dimethylbenzylamine and methyldibenzylamine. It should also be noted that E. Rochow and K. Gingold [*ibid.*, **76**, 4852 (1954)] have examined the reaction of chlorosilanes with DMF at elevated temperatures. These workers also found that carbon tetrachloride reacts violently with DMF at reflux temperature in the presence of iron powder to give a mixture of chlorinated hydrocarbons.

[5] *t*-Butyl bromide is also dehydrohalogenated in DMF containing $NaNO_2$ but at a much faster rate [N. Kornblum, H. O. Larsen, R. K. Blackwood, D. D. Mooberry, E. P. Oliveto and G. E. Graham, THIS JOURNAL, **78**, 1497 (1956).