use of D or T as label would result in a relatively smaller contribution of Ia–c in the case of T labeling. The net effect would again qualitatively account for the difference between the present results and those obtained from protonation in D_2SO_4.[10]

Experimental Section

Solvolyses and Degradations. Each reaction was carried out by passing Matheson 99% cyclopropane, purified as described by Baird and Aboderin,[7] through a sintered-glass bubbler in a gas washing bottle containing 40 ml of 9.2 *M* (20 ml of 98% H_2SO_4 and 20 ml of H_2O-*t*) or 13.8 *M* (30 ml of 98% H_2SO_4 and 10 ml of H_2O-*t*) tritiated sulfuric acid. The bubbling was allowed to continue at room temperature for 3 hr at a rate of about 30 ml of cyclopropane/min.[7] In some of the experiments, the resulting solution was heated at 50 ± 2° for 30 hr to hydrolyze any 1-propyl hydrogen sulfate,[7] while in other cases, this hydrolytic treatment was omitted. The reaction mixture was cooled and neutralized by 25% NaOH solution. Inactive 1-propanol (3.0 ml) was then added as carrier, and the resulting aqueous solution was distilled, about 5–10 ml of of distillate being collected. To the distillate 200 ml of ether was introduced, and the water present was removed by drying over anhydrous $MgSO_4$. After concentration of the ether solution, the 1-propanol was recovered by preparative vpc using a column packed with 20% Carbowax 20M on Chromosorb P.[2] The 1-propanol was degraded by oxidation to propionic acid and then to acetic acid.[2] All samples were converted to the appropriate solid derivatives, purified, and counted to give the *t* distribution as described previously.[2]

In the cases in which some 2-propanol was also formed, this alcohol, without any carrier, was separated from the 1-propanol by preparative vpc through the same Carbowax column. It was then diluted with inactive 2-propanol before being oxidized in acid dichromate to acetone.[11]

Yields of 1-Propanol from Isotope Dilution. The isotope dilution calculations were based on the following considerations. Assuming the incorporation of one proton per molecule of cyclopropane, let x = mmoles of active 1-propanol formed, then (cpm/mg ion of H^+ of the H_2SO_4-*t*)x = (x + mmoles of carrier)(cpm/mmol of the recovered 1-C_3H_7OH). Knowing the specific activities of the H_2SO_4-*t* and the recovered 1-propanol, x can be calculated.

Studies with 1-Propanol-1-*t*. Four milliliters of 1-propanol-1-*t* in 40 ml of 13.8 *M* H_2SO_4 was heated at 50 ± 2° for 30 hr. The resulting mixture was worked up as in the solvolysis of cyclopropane to give about 0.25 g of recovered 1-propanol and about 0.70 g of 2-propanol. After dilution with some carrier, the 1-propanol was degraded the usual way to give the *t* distribution.

Acknowledgment. The valuable comments of Dr. R. L. Baird and Professors N. D. Deno and C. J. Collins in regard to the present work were highly appreciated.

(10) A referee has suggested that if I were the first formed species and if there is a kinetic isotope effect in the conversion of I to II (Scheme I), then this would favor more product formation from I than from III, and one would expect an even greater excess of T at C-3 than is found in studies with D labeling. If such an effect were of greater importance than the argument that product formation from Ia–c would be smaller in the case of studies with T labeling than with D labeling, then the present results would be more in accord with II as the first formed species,[9] with kinetic isotope effect favoring its conversion to III over its conversion to I.

(11) F. G. Mann and B. C. Saunderson, "Practical Organic Chemistry," 4th ed, Longmans, Green and Co. Ltd., London, 1960, p 333.

Protonated Cyclopropanes. III. The Reactions of Lucas Reagent with Cyclopropane and with 1-Propanol[1]

C. C. Lee, W. Kao-Ying Chwang, and Kwok-Ming Wan

Contribution from the Department of Chemistry and Chemical Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada.
Received January 15, 1968

Abstract: Passage of cyclopropane through $ZnCl_2$ in 12 *M* HCl-*t* resulted in the formation of 1-chloropropane with no detectable 2-chloropropane. The *t* label was found in all three carbon positions of this product, the isotopic distribution being about 38, 19, and 43%, respectively, at C-1, C-2, and C-3. The reaction of 1-propanol-1-*t* with ordinary Lucas reagent gave chiefly 1-chloropropane with 4–6% 2-chloropropane. Degradation of this 1-chloropropane showed a total of about 1% isotope position rearrangements, the rearranged isotopic label being about equally distributed at C-2 and C-3. The roles played by equilibrating protonated cyclopropane intermediates in these two reactions and in others suggested by previous tracer work are discussed.

In the preceding paper,[2] the results of Baird and Aboderin,[3] obtained from their study on the solvolysis of cyclopropane in D_2SO_4, have essentially been confirmed by a reinvestigation using H_2SO_4-*t*. In order to explore another possibility of protonation of cyclopropane followed by ring opening product formation, the reaction of cyclopropane with Lucas reagent containing HCl-*t* has been studied. In addition, the reaction of 1-propanol-1-*t*[2] with ordinary Lucas reagent was investigated to ascertain whether protonated cyclopropane intermediates would play any role in this conversion of 1-propanol to 1-chloropropane.

Results and Discussion

Cyclopropane was passed through tritiated Lucas reagent, made up of equimolar quantities of 12 *M* HCl-*t* and $ZnCl_2$, for 24 hr at room temperature. The chloropropane formed was swept out by the excess cyclopropane and collected in cold traps containing inactive 1-chloropropane as carrier. Isotope dilution calculations showed that the yields of 1-chloropropane were of the order of 5 g. The magnitude of such yields was confirmed by inactive experiments without the use of any carrier; such inactive experiments also

(1) Supported by a grant from the National Research Council of Canada.
(2) C. C. Lee and L. Gruber, *J. Am. Chem. Soc.*, **90**, 3775 (1968).
(3) R. L. Baird and A. A. Aboderin, *ibid.*, **86**, 252 (1964).

indicated that no 2-chloropropane was produced in the reaction. The diluted active 1-chloropropane was converted into its corresponding Grignard reagent and treated with oxygen to give 1-propanol, which in turn was degraded to give the *t* distribution in the same way as previously described.[4] The results are summarized in Table I.

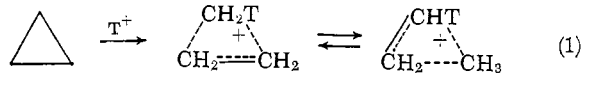
Table I. Activity Distribution in the 1-Propanol Derived from 1-Chloropropane Obtained in the Reaction of Cyclopropane with Tritiated Lucas Reagent

Run	Yield of 1-C_3H_7-Cl, g[b]	Specific activity,[a] cpm/mmol 1-C_3H_7OH[c]	CH_3CH_2-COOH[d]	CH_3-COOH[d]	*t* distribution, % C-1	C-2	C-3
1	4.6	12,300	7,550	5500	38.6	16.6	44.7
2	4.8	14,200	8,920	6120	37.2	19.7	43.1
3	5.8	16,200	10,100	7050	37.7	18.8	43.5

[a] Measured by a liquid scintillation counter. [b] Estimated by isotope dilution calculations. [c] Assayed as the α-naphthylurethan. [d] Assayed as the *p*-bromophenacyl esters.

It should be noted at this point that the data in Table I were free from complications by isotopic exchange. After ordinary 1-chloropropane was placed in the tritrated Lucas reagent for 24 hr at room temperature and then recovered, it showed no appreciable *t* activity. Reutov[5] has also found no exchange between 1-chloropropane and $ZnCl_2$ in DCl. However, Reutov and Shatkina[5,6] have reported that 1-chloropropane-1-^{14}C on being heated with $ZnCl_2$ in concentrated HCl rearranged to give solely 1-chloropropane-3-^{14}C. For example, when the mixture was heated at 50° for 100 hr, 7.5% rearrangement was observed.[6] While it would be of interest to confirm the validity of this finding of Reutov and Shatkina, in the present work, any possible effects of the Lucas reagent on the 1-chloropropane produced in the reaction would have been minimized as the product was swept out of the reaction mixture by the excess cyclopropane.

The results in Table I clearly indicated that, as in the reaction of cyclopropane with deuterated or tritiated sulfuric acid,[2,3] the isotopic label was found in all three carbon positions of the 1-propyl product, with the smallest amount of *t* label located at C-2. These data again could be explained in terms of product formation from equilibrating edge-protonated cyclopropanes, as outlined in Scheme I of the preceding paper,[2] the smaller isotopic concentration at C-2 resulting because formation of the C-2-labeled product required more extensive equilibration.[2,3] An alternative mechanism involving product formation from equilibrating methyl-bridged ions (eq 1) would also place the label at all three carbon



(1)

positions, but there is no obvious explanation of the low isotopic concentration at C-2 relative to C-1 if the reaction were to proceed only *via* eq 1 (if isotope effects were negligible).

(4) C. C. Lee and J. E. Krugor, *Tetrahedron*, 23, 2539 (1967).
(5) O. A. Reutov, *Pure Appl. Chem.*, 7, 203 (1963).
(6) O. A. Reutov and T. N. Shatkina, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 180 (1963).

Coincidentally, the *t* distribution observed in the present work (Table I) was very close to the *d* distribution noted in the reaction of cyclopropane with D_2SO_4.[3] On the other hand, the results from the reaction of cyclopropane with H_2SO_4-*t* indicated the presence of a somewhat higher amount of *t* label at C-2 and a lesser amount of *t* label at C-3. This small difference in isotopic distributions found in the reactions of cyclopropane with D_2SO_4 and with H_2SO_4-*t* has been discussed in terms of isotope effects.[2] The difference between the isotopic results from the present work (Table I) and those from the reaction of cyclopropane with H_2SO_4-*t* was probably greater than variations due to experimental errors. The higher amount of *t* label at C-3 and the lower amount at C-2 observed in the present case would suggest that the extent of equilibration was smaller, or the "lifetime" of the protonated cyclopropane intermediates was shorter, in the case of the reaction of cyclopropane with Lucas reagent than in the corresponding reaction with H_2SO_4. The present results also differed from those reported in the preceding paper[2] in the much greater yield of 1-chloropropane than the yield of 1-propanol. A chief factor responsible for this difference was obviously the longer reaction time utilized in the present experiments.

Reaction of 1-propanol-1-*t* with Lucas reagent gave a product consisting of chiefly 1-chloropropane with 4–6% 2-chloropropane. This mixture was converted into the corresponding Grignards and treated with oxygen and the resulting alcohols were separated by preparative vpc.[4] The 1-propanol so obtained was degraded in the usual way to give the results shown in Table II. It may be noted from Table II that 99% of the *t* label remained unrearranged at C-1. Of the small portion of *t* label that has rearranged, the data could be regarded as showing nearly equal amounts of rearrangement to C-2 and C-3, suggesting that a small proportion of the reaction likely has proceeded *via* essentially completely equilibrated protonated cyclopropane intermediates.

Table II. Activity Distribution in the 1-Propanol Derived from 1-Chloropropane Obtained in the Reaction of 1-Propanol-1-*t* with Lucas Reagent

Run	Specific activity,[a] cpm/mmol 1-C_3H_7OH[b]	CH_3CH_2-COOH[c]	CH_3-COOH[c]	*t* distribution, % C-1	C-2	C-3
1	122,000	990	470	99.19	0.42	0.39
2	446,000	3,770	1,690	99.15	0.47	0.38
3	14,100,000[d]	148,000[d]	68,900[d]	98.95	0.56	0.49

[a] Measured by a liquid scintillation counter. [b] Assayed as the α-naphthylurethan. [c] Assayed as the *p*-bromophenacyl esters. [d] Absolute number of dpm/mmol.

The magnitudes of the isotopic rearrangements recorded in Table II, though small, should be quite reliable as similar results were obtained from reactants of widely different specific activities. These results were also shown to be free from complications by isotopic exchange. When ordinary 1-propanol was treated with tritiated Lucas reagent and the product converted into the Grignard and treated with oxygen, the 1-propanol isolated by preparative vpc contained no appreciable *t* activity. The over-all rearrangement of about 1% to C-2 and C-3 in the reaction of 1-propa-

Table III. Summary of Observations

Reaction	Proportion of 2-propyl relative to 1-propyl products	Extent of reaction *via* protonated cyclopropanes	Amount of label at C-2 relative to C-3 in 1-propyl product[e]
1. c-C_3H_6 + H_2SO_4-t[a]	None	Complete	Smaller
2. c-C_3H_6 + $ZnCl_2$–HCl-t[b]	None	Complete	Smaller
3. 1-t- or 1-^{14}C-1-$C_3H_7NH_2$ + HNO_2[c]	Large	Small	About equal
4. 1-t-1-C_3H_7OH in 13.8 M H_2SO_4 at 50°[a]	Large	Small	About equal
5. 1-^{14}C-1-C_3H_7OTs + HCOOH[d]	Small	Very small	Smaller
6. 1-t-1-C_3H_7OH + $ZnCl_2$–HCl[b]	Small	Very small	About equal

[a] Reference 2. [b] The present work. [c] Reference 4. [d] Reference 7. [e] In reactions 3, 4, and 6, because of the small amounts of rearrangement, a differentiation between about equal and the statistical distribution of 2:3 for the t label at C-2 and C-3 was not attempted.

nol-1-t with Lucas reagent was comparable to the approximately 0.8% rearrangement to C-2 and C-3 observed in the formolysis of 1-propyl-1-^{14}C tosylate;[7] however, in the formolysis reaction, the rearranged isotopic label was not equally distributed at C-2 and C-3.

Summarized in Table III are some observations from tracer studies on various reactions in which protonated cyclopropane intermediates likely have played some role. For reactions 1 and 2 in which cyclopropane was one of the reactants, the exclusive formation of 1-propyl products indicated that the classical 1-propyl cation likely was not involved, otherwise some 2-propyl products would have been found. The inequality in the amounts of isotopic label at C-2 and C-3 suggested that equilibration was taking place among the protonated cyclopropane intermediates and that complete equilibration has not been attained before the intermediates reacted with nucleophiles to give the products. A similar course of reaction involving equilibrating substituted protonated cyclopropanes has been reported in the Lewis acid catalyzed reaction of cyclopropane with acetyl chloride[8] or with bromine.[9]

Reactions 3–6 (Table III) involved aliphatic 1-propyl compounds instead of cyclopropane. In these cases, only minor fractions of the over-all reactions proceeded through protonated cyclopropane intermediates. In the deamination of 1-propylamine and in the heating of 1-propanol in 13.8 M H_2SO_4 (reactions 3 and 4), the formation of large amounts of 2-propanol suggested that the classical 1-propyl cation, which could undergo 1,2-hydride shift, was of predominant importance. The similarity in the loss of stable N_2 from the diazonium ion and the loss of stable H_2O from the conjugate acid of 1-propanol could result in a 1-propyl cation of sufficiently high energy that a small fraction of it could convert into protonated cyclopropane which completely equilibrated before giving rise to product.

The formolysis of 1-propyl tosylate and the reaction of 1-propanol with Lucas reagent (reactions 5 and 6) both gave chiefly 1-propyl products. In reaction 5, only 1–2% 2-propyl formate was obtained[7] and in reaction 6, about 4–6% 2-chloropropane was found. The total isotopic rearrangement to C-2 and C-3 in these two cases was also very small, being of the order of about 1%. These features indicated that a large component in each of these two reactions was of the SN2 type or its equivalent.[7,10] In reaction 6, the SN2 process could involve a species such as I[11] reacting with chloride ion. It is also generally recognized that under solvolytic conditions, any carbonium ion formed would be less energetic than that from a reaction such as deamination. Thus in reaction 5, that component which involved protonated cyclopropane intermediates would not be expected to behave like the protonated cyclopropanes in the deamination. It is, therefore, not surprising that in the formolysis, the portion of product that resulted from protonated cyclopropanes showed a smaller isotopic concentration at C-2, indicating incomplete equilibration of the intermediates. In the reaction of 1-propanol with Lucas reagent, the ionic process involving protonated cyclopropanes could arise in a way quite similar to the formation of protonated cyclopropanes during the heating of 1-propanol in H_2SO_4 (reaction 4). Thus in both reactions 4 and 6, the isotopic concentrations at C-2 and C-3 were approximately equal, pointing to a more complete equilibration of the protonated cyclopropane intermediates.

$$\begin{array}{c} CH_3CH_2CHTO\ldots ZnCl_2 \\ \quad\quad\quad\quad\quad\quad | \\ \quad\quad\quad\quad\quad\quad H \\ \quad\quad\quad\quad\quad\quad I \end{array}$$

Experimental Section

Reaction of Cyclopropane with Tritiated Lucas Reagent. Purified cyclopropane[2] was passed through a sintered-glass bubbler into 40.8 g (0.3 mol) of $ZnCl_2$ in 25 ml (0.3 mol) of 12 M HCl-t for 24 hr at room temperature. The product was swept out by the excess cyclopropane and collected in two cold traps (Dry Ice–acetone), the first of which contained 10 ml of ordinary 1-chloropropane as carrier. The recovered material was dried over anhydrous Na_2CO_3 and $MgSO_4$ and distilled before it was subjected to degradation. In trials with inactive Lucas reagent without the use of any carrier, the product obtained was tested in a 25-ft analytical vpc column packed with 25% β,β'-oxydipropionitrile on Chromosorb G and found to contain only 1-chloropropane with no detectable 2-chloropropane.

Reaction of 1-Propanol-1-t with Lucas Reagent. A mixture of 3.0 g (0.05 mol) of 1-propanol-1-t and 13.6 g (0.1 mol) of $ZnCl_2$ in 8.3 ml (0.1 ml) of 12 M HCl was heated in an oil bath under reflux for 1 hr. The product was then distilled from the reaction mixture, the material boiling up to 50° being collected. After drying over anhydrous Na_2CO_3 and $MgSO_4$, the yield of recovered products amounted to about 50%. Analysis in the 25-ft β,β'-oxydipropionitrile column showed that the product was 1-chloropropane containing 4–6% 2-chloropropane.

Degradations. Samples of the 1-chloropropane from the reaction of cyclopropane with tritiated Lucas reagent or of the mixture of 1-chloropropane and 2-chloropropane from the reaction of 1-pro-

(7) C. C. Lee and J. E. Kruger, *Can. J. Chem.*, 44, 2343 (1966).
(8) H. Hart and R. H. Schlosberg, *J. Am. Chem. Soc.*, 88, 5030 (1966).
(9) N. C. Deno and D. N. Lincoln, *ibid.*, 88, 5357 (1966).
(10) A. Streitwieser, Jr., *ibid.*, 77, 1117 (1955).
(11) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p 392.

panol-1-t with ordinary Lucas reagent were converted into the corresponding Grignard reagents. Each sample was cooled in an ice bath while oxygen was bubbled into the reaction mixture for 1 hr. The resulting material was decomposed by the addition of dilute HCl and then subjected to continuous extraction with ether for 24 hr. After drying and the removal of most of the ether, the residue was purified by preparative vpc[4] to give pure 1-propanol. When necessary, inactive 1-propanol was added as carrier before it was degraded by oxidization to propionic acid and then acetic acid as previously described.[4] In preliminary trials using inactive materials, the conversion of 1-chloropropane to 1-propanol was found to proceed in yields of 50–60%.

Kinetics of Proton Transfer from the α Carbon of Ethyl Thioacetate and Its Dimethyliminium Derivative[1]

Gustav E. Lienhard and Tung-Chia Wang

Contribution from the James Bryant Conant Laboratory, Harvard University, Cambridge, Massachusetts 02138. *Received January 15, 1968*

Abstract: Rate constants at 25° for the hydrolysis of and enamine formation from ethyl N,N-dimethylthioacetimidate, $CH_3C(=N^+(CH_3)_2)SC_2H_5$, have been determined. Both reactions are catalyzed by general bases; enamine formation occurs more rapidly than hydrolysis. The rate constant for abstraction of a proton by hydroxide ion from the α carbon of ethyl thioacetate at 25° has also been determined. Comparison of this rate constant with that for the analogous reaction of ethyl N,N-dimethylthioacetimidate shows that $C(=N^+(CH_3)_2)SR$ activates an α-hydrogen atom for proton transfer to hydroxide ion about 2×10^4 times better than C(=O)SR.

The kinetic acidity of the α-hydrogen atoms of simple thiol esters has not previously been determined. In this paper we describe the determination of the rate constant for the abstraction by hydroxide ion of an α-hydrogen atom from ethyl thioacetate, based upon a method of tritium–hydrogen exchange. In addition, in order to compare the effect of the dimethyliminium function with the carbonyl function, we have measured the rates of base-catalyzed enamine formation from ethyl N,N-dimethylthioacetimidate ($CH_3C(=N^+(CH_3)_2SC_2H_5$) and also determined the kinetics of hydrolysis of this compound. In the Discussion we consider the relevance of our results to the mechanisms of enzymatic reactions which involve reaction at the α carbon of thiol esters.

Experimental Section

Materials. Ethyl thioacetate was purchased from J. T. Baker Chemical Co. and redistilled before use. 1,1-Cyclobutanedicarboxylic acid was recrystallized from ethyl acetate–1,2-dichloroethane (1:3).

Ethyl N,N-dimethylthioacetimidate bromide was prepared by the reaction of N,N-dimethylthioacetamide with ethyl bromide.[2] In a typical preparation, N,N-dimethylthioacetamide (3.5 g) was refluxed with ethyl bromide (11 ml) in dry acetone (12 ml) for 21 hr, with stirring. Enough anhydrous ether was then added to precipitate completely the product, which was collected, washed thoroughly with anhydrous ether, and dried and stored over phosphorus pentoxide in an evacuated desiccator; 5.2 g (74% of theory) of a white crystalline deliquescent solid, mp 139–141° (with gas evolution), was obtained. *Anal.* Calcd for $C_6H_{14}BrNS$: C, 33.97; H, 6.65; Br, 37.66; N, 6.60. Found: C, 33.74; H, 6.65; Br, 37.73; N, 6.63. The ultraviolet spectrum of a freshly prepared solution in 10^{-2} N HCl, taken before the thioacetimidate had undergone more than 1% hydrolysis, showed λ_{max} 254 mμ (ε 11,000). This spectrum is similar to that reported[3] for protonated thioacetimidic acid ethyl ester in water (λ_{max} 243 mμ (ε 9950)). The proton magnetic resonance (pmr) spectrum of a freshly prepared 0.2 M solution in 10^{-4} N DCl in D_2O had signals at δ 1.39 (triplet, J = 7.5 Hz, 3 H, CH_3CH_2), 2.66 (singlet, 3 H, $CH_3C(=N)S$), 3.31 (quartet, J = 7.5 Hz, 2 H, CH_3CH_2S), and 3.48 and 3.55 (two singlets, 6 H, $N(CH_3)_2$). This and all other pmr spectra were taken on a Varian A-60 spectrometer operating at 60.00 MHz. Chemical shifts (δ in parts per million) are relative to the external standard of tetramethylsilane in chloroform.

Kinetic Measurements. The rates of hydrolysis of ethyl N,N-dimethylthioacetimidate in hydrochloric acid, potassium acetate, potassium 1,1-cyclobutanedicarboxylate, and potassium phosphate buffers were followed spectrophotometrically at 260 mμ. Each reaction was initiated by the addition of a small volume (0.5 ml or less) of a freshly prepared concentrated solution of the iminium compound in 10^{-4} N HCl to 80 ml of a temperature-equilibrated solution of buffer and potassium chloride (a sufficient amount to give an ionic strength of 0.5 M) in a stoppered 100-ml volumetric flask. The reaction mixtures, which initially contained 10^{-4} M iminium compound, were maintained at 25.0° in a water bath. At various times a 3-ml aliquot was removed from each reaction mixture and its absorbance immediately measured at 260 mμ with a Zeiss PMQ II spectrophotometer against a blank the composition of which was identical with the reaction mixture except for the omission of the iminium compound. The hydrolyses were followed for at least two half-times, and the first-order rate constants were calculated from the resulting linear semilogarithmic plots of absorbance against time by use of the relationship $k_{obsd} = 0.69/t_{1/2}$. This procedure was altered slightly in measuring the faster rates of hydrolysis in potassium carbonate, triethylenediamine (1,4-diazabicyclo[2.2.2]octane), and imidazole buffers. In these cases reaction mixtures were contained in stoppered 3-ml, 1-cm cuvettes placed in the thermostated cell holder of the spectrophotometer. The absorbance at 270 or 253 mμ relative to water in the blank cuvette was recorded as a function of time, and the first-order rate constants were obtained from the linear semilogarithmic plots of $A_t - A_\infty$ against time, where A_t is the absorbance at time t and A_∞ is the final absorbance.

The rates of reaction of iodine with ethyl N,N-dimethylthioacetimidate were determined by measuring the decrease in absorbance of triiodide ion at 351 mμ.[4] The reaction mixtures contained the iminium thiol ester (5×10^{-2}–10^{-3} M), buffer (0.005–0.030 M), potassium iodide (0.005 M), sufficient potassium chloride to give an ionic strength of 0.5 M (0.43–0.48 M), and iodine (as I_2, I_3^-, I_2Br^-, and I_2Cl^-; initially 4×10^{-5} or 8×10^{-5} M). All these components except the iminium compound were prepared in

(1) This research was supported by a grant (GB 4848) from the National Science Foundation. Address inquiries to G. E. L.

(2) D. A. Peak and F. Stansfield, *J. Chem. Soc.*, 4067 (1952).

(3) G. E. Lienhard and W. P. Jencks, *J. Am. Chem. Soc.*, 87, 3863 (1965).

(4) E. T. Harper and M. L. Bender, *ibid.*, 87, 5625 (1965).