retention time was assigned the *dl* structure (see Results): nmr ($CDCl_3$) δ 7.3–6.8 (m, 5) and 4.0 (m, 1);[24] mp 73–75°.

Anal. Calcd for $C_{16}H_{12}F_6$: C, 60.35; H, 3.82. Found: C, 60.49; H, 3.90.

The product with the longer retention time was assigned the meso structure (see Results): nmr ($CDCl_3$) δ 7.4 (s, 5) and 4.0 (m, 1);[24] mp 156–158°.

Anal. Calcd for $C_{16}H_{12}F_6$: C, 60.35; H, 3.82. Found: C, 60.42; H, 3.84.

In a large-scale run, the combined pyrolysate from 30 g of oxalate, pyrolyzed in 3-g portions at 650°, was dissolved in hot ethanol. Upon cooling, the impure meso isomer separated as white crystals, mp 160–162°, leaving the ethanol rich in the *dl* isomer. Recrystallization of these crystals from ethanol gave 5 g of the meso isomer, mp 161–162°. Evaporation of the initial mother liquor gave a residue which, when recrystallized from petroleum ether (bp 30–60°), gave 3 g of white crystals, mp 65–70°. This low-melting material was further purified by chromatography on alumina using petroleum ether as the eluent giving white crystals of the *dl* isomer, mp 72–74°.

Single crystals of the high-melting isomer suitable for X-ray diffraction were grown by slow evaporation of a petroleum ether (bp 30–60°) solution. These crystals melted at 161–162°. A crystal of approximate dimension 0.2 mm on an edge was chosen and mounted along the *a* axis. Weissenberg photographs were taken with Ni-filtered Cu K_α radiation (1.5418 Å) of the 0*kl* and 1*kl* zones. A second crystal was mounted and the *h*0*l* and *h*1*l* zones were recorded.

The ratio of the two DPHFB isomers obtained from a pyrolysis at 500° was based on glpc analysis. The thermal conductivities of the two isomers were found to be identical. The absolute yield of the DPHFB isomers was obtained from the pyrolysate based on nmr analysis using bibenzyl as an internal standard. Less than 5% *dl*-DPHFB was obtained when *meso*-DPHFB was passed through the pyrolysis apparatus with the furnace heated to 500°.

Pyrolysis of Di-α-pentafluoroethylbenzyl Oxalate.—Pyrolysis of di-α-perfluoroethylbenzyl oxalate took place at 650° with a head temperature of 135–140°. The characteristic nmr spectrum of the β,β-difluorostyrene was the main feature of the nmr spectrum of the pyrolysate.[25] The yield of β,β-difluorostyrene was determined by nmr analysis using bibenzyl as an internal standard. Glpc analysis of the pyrolysate showed the presence of at least three high-boiling components in small amounts (column A).

Pyrolysis of di-α-trichloromethyl oxalate was carried out at 500 and 680° at 10^{-4}–10^{-5} mm with a head temperature of 135°.[6] The nmr spectrum (CCl_4) of the pyrolysate showed essentially a single product, β,β-dichlorostyrene, present in 32% yield relative to an internal standard, 1,1,2,2-tetrachloroethane (δ 6.00): nmr (CCl_4) δ 7.37 (m, 5, C_6H_5) and 6.78 (s, 1, $CH{=}CCl_2$) [lit.[26] nmr ($CDCl_3$) δ 7.25 (m, 5) and 6.72 (s, 1)]. Glpc analysis of the product mixture (column B) showed one main peak and several smaller peaks, the smaller peaks accounting for less than 5% of the crude mixture assuming equal thermal conductivities. A mass spectrum of the crude mixture gave a parent ion peak at *m/e* 172.

Pyrolysis of Di-α,α-dimethylbenzyl Oxalate.—The nmr spectrum of the pyrolysate run at 340° showed exclusively the characteristic spectrum of α-methylstyrene. Nmr analysis using bibenzyl as an internal standard showed that a quantitative yield of the styrene was obtained. The identity of the product was further confirmed by glpc analysis (column B).

Registry No.—Di-α,α-dimethylbenzyl oxalate, 31164-25-7; *dl*-DPHFB, 31208-74-9; *meso*-DPHFB, 31164-26-8.

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[24] The appearance of the nmr signal for the aromatic protons of DPHFB is highly solvent dependent (unpublished work by W. S. T., J. G. P., and F. L. W.).

[25] S. A. Fuqua, W. G. Duncan, and R. M. Silverstein, *J. Org. Chem.*, **30**, 1027 (1965).

[26] E. Kiehlmann, R. J. Bianchi, and W. Reeve, *Can. J. Chem.*, **47**, 1521 (1969).

The Thermal Decomposition of β-Hydroxy Esters

B. L. YATES,* A. RAMIREZ, AND O. VELASQUEZ

Departamento de Quimica, Universidad del Valle, Cali, Colombia

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The products and kinetics of the thermal decomposition of several β-hydroxy esters have been studied. It has been shown that all of the β-hydroxy esters studied pyrolyze to form a mixture of the corresponding ester and aldehyde or ketone and that the decomposition follows first-order kinetics and appears to be homogenous and unimolecular. Based on these data a six-membered cyclic transition state is proposed for the reaction. The absence of large substituent effects indicates that little charge separation occurs during the breaking of the carbon–carbon double bond.

It has recently been shown[1] that ethyl 3-hydroxy-3-methylbutanoate decomposes thermally in xylene solution to a mixture of acetone and ethyl acetate (eq 1).

$$(CH_3)_2COHCH_2CO_2C_2H_5 \longrightarrow (CH_3)_2C{=}O + CH_3CO_2C_2H_5 \tag{1}$$

It was proposed that the reaction involves a cyclic six-membered transition state similar to that thought to be involved in other similar thermal decomposition reactions such as the thermolysis of β-hydroxy ketones,[2] β-hydroxy olefins,[3] β-hydroxy alkynes,[4] and esters.[5] The present paper reports the products and kinetics of the thermolysis in the gas phase of several other β-hydroxy esters.

Results

The β-hydroxy esters listed in Table I were pyrolyzed in evacuated, sealed glass tubes. All of the β-hydroxy esters pyrolyzed to a mixture of the ester and aldehyde or ketone according to eq 2.

$$R_2COHCHRCO_2C_2H_5 \longrightarrow R_2CO + RCH_2CO_2C_2H_5 \tag{2}$$

The products of the reaction were identified by their glc retention times and by the formation of 2,4-dinitrophenylhydrazones of the aldehyde or ketone from the products of the reaction. No other major products of reaction were observed by glc, and quantitative glc measurements using *p*-xylene as an internal standard indicated that the above reaction occurred to at least 90% for all of the β-hydroxy esters studied. No peak due to water was observed indicating that under the conditions of reaction no dehydration occurred. Also in the case of the ethyl esters no peak due to ethylene was observed indicating that a possible side reaction, the pyrol-

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[1] B. L. Yates and J. Quijano, *J. Org. Chem.*, **35**, 1239 (1970).

[2] B. L. Yates and J. Quijano, *ibid.*, **34**, 2506 (1969).

[3] G. G. Smith and B. L. Yates, *J. Chem. Soc.*, 7242 (1965).

[4] A. Viola, J. H. MacMillan, R. J. Proverb, and B. L. Yates, *J. Amer. Chem. Soc.*, in press.

[5] C. H. DePuy and R. N. King, *Chem. Rev.*, 431 (1960).

TABLE I

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE PYROLYSIS OF SOME β-HYDROXY KETONES

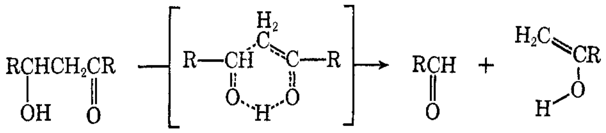
Compd	Registry no.	Temp, °C	10^4k, sec^{-1}	E_a, kcal/mol	$\log_{10} A$	$\Delta S^{\ddagger}$, eu
Ethyl 3-hydroxybutanoate	5405-41-4	340	6.98			
		330	4.13	39.7	10.98	−11.7
		320	2.32			
		310	1.32			
Ethyl 3-hydroxy-2-methylbutanoate	27372-03-8	330	12.6			
		320	7.45	39.0	11.25	−10.4
		310	4.12			
		300	2.34			
Ethyl 3-hydroxy-3-methylbutanoate	18267-36-2	320	10.2			
		310	5.73	38.5	11.20	−10.6
		300	3.30			
		290	1.78			
Methyl 3-hydroxy-3-methylbutanoate	6149-45-7	320	9.10			
		310	5.12	39.1	11.34	−10.0
		300	2.80			
		290	1.55			
Ethyl 3-phenyl-3-hydroxypropionate	5764-85-2	280	3.23			
		270	1:69	38.1	11.57	−9.0
		260	0.877			
		250	0.445			

ysis of the ester[5] involving the $-OC_2H_5$ group, takes place to a negligible degree at the temperature of the reaction.

The kinetics of the thermolysis were followed by glc using *p*-xylene as an internal standard. Visual observation of the hot capillary tubes confirmed that the sample was completely vaporized at the temperature of the reaction, except in the case of the ethyl 3-phenyl-3-hydroxypropionate. This compound pyrolyzed at too low a temperature to be vaporized and its rate of pyrolysis was determined in the liquid phase by sealing in the capillaries a sample of sufficient size so that all remained in the liquid state (see Experimental Section). Good first-order kinetics were observed for the thermolysis of all the β-hydroxy esters, the reaction being followed both by the rate of appearance of the products as by the rate of disappearance of the β-hydroxy ester. Identical rate constants were obtained, and in all cases plots of $\log_{10} C/C_0$ were found to be linear to at least 3 half-lives. The rate constants obtained are listed in Table I. They were found to be reproducible to within ±5%. No variation in rate constant was obtained by using different concentrations of the β-hydroxy ester in toluene (in the range of 1–10% of ester by volume) nor by sealing different sample sizes in the capillaries (as long as the sample size was sufficiently small that all was completely vaporized). The reaction was shown to be homogeneous by increasing the surface area of the reaction vessel. Thus, in the case of ethyl 3-hydroxy-3-methylbutanoate, a rate constant of 1.04×10^{-3} sec^{-1} was obtained at 320° in glass tubes packed with capillary tubing, which increased the surface area by a factor of five, compared to 1.02×10^{-3} in unpacked tubes. All Arrhenius plots showed excellent linearity. The calculated energies and entropies of activation are listed in Table I. They are estimated to be accurate to within ±1.2 kcal and ±1.8 eu, respectively.

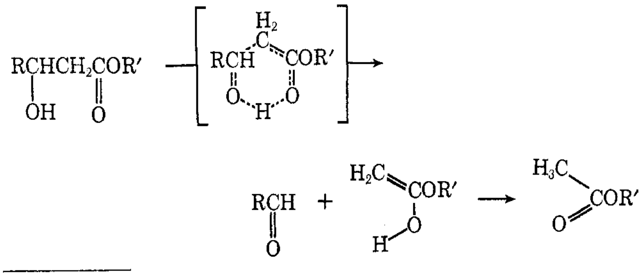
Discussion

It has previously been shown[2] that β-hydroxy ketones pyrolyze to mixtures of aldehydes and ketones and, based on the products and kinetics of the reaction, a cyclic transition state was proposed for the reaction.



This mechanism was further supported by the observation[6] that the bicyclic compound, 3,3-dimethyl-1-(1-hydroxy-1-methylethyl)bicyclo[2.2.1]heptanone, which cannot form a cyclic transition state without forming a double bond at the bridgehead is essentially stable to heat.

The results obtained in the present study suggest that the pyrolyses of β-hydroxy esters and β-hydroxy ketones are closely related. Thus β-hydroxy esters pyrolyze to mixtures of esters and aldehydes or ketones, these being products that would be expected if the reaction followed a mechanism similar to that proposed for the β-hydroxy ketone pyrolysis. Furthermore, the kinetics obtained for the pyrolysis of the β-hydroxy esters are very similar to those obtained for the pyrolysis of β-hydroxy ketones; both reactions appear to be homogeneous and monomolecular with negative entropies of activation in the range of −8.7 to −12.6 eu. These values are typical of unimolecular reactions that are thought to involve cyclic transition states.[7] On these bases it is proposed that β-hydroxy esters pyrolyze through a six-membered



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[6] T. Mole, *Chem. Ind.* (*London*), 1164 (1960).

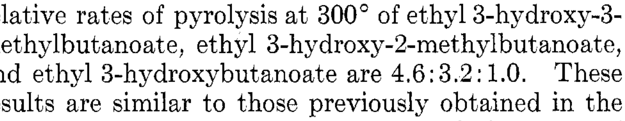
[7] S. W. Benson, "The Foundation of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 257.

transition state similar to that previously proposed for the pyrolysis of β-hydroxy ketones.

It was previously observed that[3] in xylene solution at 200° the β-hydroxy ketone, 4-hydroxy-4-methyl-2-pentanone, pyrolyzes 360 times more rapidly than the analogously substituted β-hydroxy ester, ethyl 3-hydroxy-3-methylbutanoate. In the present study this behavior is confirmed; all of the β-hydroxy esters pyrolyze much more slowly than the correspondingly substituted β-hydroxy ketone. In particular, in the gas phase at 300° 4-hydroxy-4-methyl-2-pentanone pyrolyzes 630 times[7] as fast as ethyl 3-hydroxy-3-methylbutanoate. The mechanism proposed above is consistent with this greater ease of pyrolysis of the β-hydroxy ketones given the greater difficulty of formation of the enol form of esters than of ketones.[1,8]

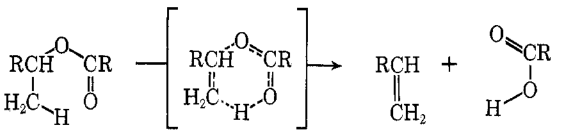
Furthermore, as would be expected[9] for an intramolecular unimolecular reaction, the effect of a nonpolar solvent on the velocity of pyrolysis of the β-hydroxy esters is small. Thus the energy and entropy of activation for pyrolysis of ethyl 3-hydroxy-3-methylbutanoate in xylene solution at 200° are 37.9 kcal and −10.7 eu and, for the same reaction in the gas phase at 300°, 38.5 kcal and −10.6 eu. These activation parameters give extrapolated rate constants for the reaction in solution and in the gas phase at 250° of 6.3×10^{-5} and 1.7×10^{-5} sec^{-1}. Similarly, the effect of solvent was found to be small in the pyrolysis of β-hydroxy ketones. For the pyrolysis of 4-hydroxy-4-methyl-2-pentanone at 200°, rate constants of 5.4 and 6.8×10^{-4} sec^{-1} were obtained for the reaction in the gas phase and in xylene solution, respectively.

On comparing the relative rates of pyrolysis of the β-hydroxy esters given in Table I, it can be seen that the effect of methyl groups on the ease of breaking of the carbon–carbon bond appears to be small. Thus the relative rates of pyrolysis at 300° of ethyl 3-hydroxy-3-methylbutanoate, ethyl 3-hydroxy-2-methylbutanoate, and ethyl 3-hydroxybutanoate are 4.6:3.2:1.0. These results are similar to those previously obtained in the pyrolysis of β-hydroxy ketones;[2] the relative rates of pyrolysis of 4-hydroxy-4-methyl-2-pentanone, 4-hydroxy-3-methyl-2-pentanone, and 4-hydroxy-2-pentanone are 2.9:1.9:1.0. Similar small effects of methyl groups on the breaking carbon–carbon bond are found in the pyrolysis of β-hydroxy olefins[3] and β-hydroxy alkynes,[4] both of which reactions are thought to involve similar cyclic transition states.



The relative rates of pyrolysis at 350° of the β-hydroxy olefins 3-buten-1-ol, 4-penten-2-ol, and 2-methyl-4-penten-2-ol are 1:2.9:5.5,[3] and of the β-hydroxy acetylenes 3-butyn-1-ol, 4-pentyn-2-ol, and 2-methyl-4-pentyn-2-ol are 1:2.0:2.5.

On the other band, in the pyrolysis of esters the effect of substitution on the breaking carbon–oxygen bond is much more marked.



The rates of pyrolysis of ethyl, isopropyl, and *tert*-butyl acetates are 1:19:1170.[5] Although part of this effect is statistical, there being more hydrogens available for reaction in the case of the more highly branched esters, the effect is too big to be accounted for solely on this basis, and it has been suggested[10] that some carbonium ion character is developed on the carbon atom during the breaking of the carbon–oxygen bond. The much smaller effect of methyl substitution in β-hydroxy ester pyrolysis would thus seem to indicate much less charge separation during the breaking of the carbon–carbon bond, which is reasonable when it is considered that in the breaking of the carbon–oxygen bond in ester pyrolysis two atoms of different electronegativity are involved.

The 3-phenyl group has a small accelerating effect on the rate of pyrolysis of the β-hydroxy esters. Thus the relative rates of pyrolysis at 300° of ethyl 3-phenyl-3-hydroxypropionate and ethyl 3-hydroxybutanoate are 15:1. Part of this accelerating effect is due to the fact that the pyrolysis of ethyl 3-phenyl-3-hydroxypropionate was carried out in the liquid phase. Nevertheless, this cannot account for all of the increased rate of pyrolysis of the phenyl compound. The extrapolated values for the rate of pyrolysis of ethyl 3-hydroxy-3-methylbutanoate in the gas phase and in xylene solution at 250° are 1.7×10^{-5} and 6.3×10^{-5}; that is, in the liquid phase the reaction is about three times as fast as in the gas phase. Furthermore, the rates of pyrolysis of ethyl 3-hydroxy-3-methylbutanoate and ethyl 3-phenyl-3-hydroxypropionate in xylene solution at 250° are 6.3×10^{-5} and 4.45×10^{-5} sec^{-1}, respectively. That is, a phenyl group joined to the carbinol carbon has about five times the accelerating effect on the rate of pyrolysis as a methyl group in a similar position and about the same effect as two methyl groups. A similar accelerating effect of a phenyl group has been noted in the case of β-hydroxy olefins and β-hydroxy acetylenes. Thus, 1-phenyl-3-buten-1-ol pyrolyzes 7.5 times as fast as 4-penten-2-ol and 1-phenyl-3-butyn-1-ol pyrolyzes 6.2 times as fast as 4-pentyn-2-ol. It is difficult to say whether this small accelerating effect of a phenyl group on β-hydroxy ester pyrolysis is due to stabilization of the transition state by conjugation with the forming carbonyl group or stabilization of a partial positive charge on the carbinol carbon. Nevertheless, it is notable that in ester pyrolysis in which the transition state would appear to be much more polarized, a similarly substituted phenyl group has a much greater effect, the relative rates of pyrolysis at 300° of 1-phenylethyl acetate and ethyl acetate being 58:1.[11]

Finally, as would be expected and as can be seen from Table I, little difference is observed between the rates of thermolysis of methyl and ethyl esters. Thus the rates of pyrolysis at 300° of ethyl 3-hydroxy-3-methylbutanoate and methyl 3-hydroxy-3-methylbutanoate are 3.30 and 2.80×10^{-4} sec^{-1}, respectively.

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[8] J. March, "Advanced Organic Chemistry: Reactions, Mechanisms and Structure," McGraw-Hill, New York, N. Y., 1968, p 60.

[9] See ref 7, p 506.

[10] G. G. Smith, F. D. Bagley, and R. Taylor, *J. Amer. Chem. Soc.*, **83**, 3047 (1961).

[11] R. Taylor, G. G. Smith, and W. H. Wetzel, *ibid.*, **84**, 4817 (1962).

The results of this study thus indicate that β-hydroxy esters pyrolyze to mixtures of the corresponding ester and aldehyde or ketone and that the reaction involves a cyclic transition state, which owing to the comparatively small substituent effects observed, most probably is concerted.

Experimental Section

β-Hydroxy Esters.—Ethyl 3-hydroxybutanoate was bought (Aldrich Chemical Co.); the other β-hydroxy esters were prepared by the Reformatsky reaction[12] between the appropriate aldehyde or ketone and α-bromo ester. All of the esters were distilled carefully before use and their purity checked by glc. The physical properties (boiling point and refractive index) of all the esters prepared agree closely with literature values.

Thermolysis of the β-Hydroxy Esters.—Thermolysis of the esters were carried out in carefully washed glass tubes, 2-mm i.d. and 40–50-mm length. The ester (20 μl) was placed in the tube, the contents were frozen in Dry Ice–acetone, and the tube was evacuated, flushed several times with nitrogen, and finally evacuated and sealed. The tubes were then placed in a heated aluminum block (see the kinetic measurements), and thermolyzed during 4 or 5 half-lives. At the end of the reaction, the tubes were cooled in Dry Ice–acetone, and a sample was withdrawn and analyzed by glc using a 5-ft SE-30 column. A further sample was withdrawn and added to a solution of 2,4-dinitrophenylhydrazine in phosphoric acid,[13] and the resulting 2,4-dinitrophenylhydrazone was filtered and crystallized and its melting point was determined.

Kinetic Procedures.—The kinetic methods used were those described previously.[4] ACS reagent grade toluene was used without further purification. p-Xylene (Aldrich Chemical Co.) was refluxed over sodium and then fractionated. Thermolyses were carried out in a heated aluminum block 14 in. long by 8 in. in diameter insulated by glass wool. The block was heated by a resistance coil and its temperature controlled to ±0.2° by a Fielden type TCB2 temperature controller. The absolute temperature was checked by a chromel–alumel thermocouple. Approximately 10–15 μl of a solution of the β-hydroxy ester (4% v/v) and p-xylene (2% v/v) in toluene was injected through a rubber septum into a nitrogen-filled capillary, 2-mm i.d. and 40–50-mm length. The capillary was then sealed. Five such capillaries were placed in holes drilled in the block, the holes being of such diameter that the tubes fitted precisely, and at determined intervals the tubes were withdrawn and the reaction was quenched by quickly plunging them into cold water. The contents of the tubes were analyzed by glc using a 5-ft SE-30 column at 180° for the phenyl ester and 100° for the other esters. Under these conditions retention times of 1–2 min were observed. The areas of the peaks due to the starting β-hydroxy ester and the standard p-xylene were compared using a Photovolt Model 49 integrator. In the case of ethyl 3-hydroxy-3-methyl butanoate, the reaction was also followed at various temperatures by comparing the areas of the peaks due to ethyl acetate and acetone (the products of the reaction) with that of the standard p-xylene. Identical rate constants were obtained as by the former method.

The validity of this method was established by a determination of the rates of pyrolysis of 2-methyl-4-penten-2-ol at 330 and 320°. Rates of 10.5 and 6.20 $\times 10^{-4}$ sec^{-1} were obtained compared to extrapolated literature values[3] of 11.1 and 6.31 $\times 10^{-4}$ sec^{-1}. In the case of ethyl 3-phenyl-3-hydroxypropionate, decalin (refluxed over sodium and fractionated) was used as an internal standard, the reaction was studied in the liquid phase. Sufficient solution (50–100 μl) of the ethyl 3-phenyl-3-hydroxypropionate in toluene was injected into the capillary so that the capillary was about half full. Under these conditions all of the sample remained in the liquid phase. A sample placed in the hot block showed no decrease in volume but rather an increase due to the thermal expansion of the sample.

Quantitative measurement of the yield of the products of reaction was carried out under the same conditions as for the kinetic measurements, but the reaction mixture was pyrolyzed during 4–5 half lives and then analyzed by glc using a 5-ft SE-30 column. The areas of the peaks obtained were compared to those obtained from a known mixture of the aldehyde or ketone, ester, and p-xylene in toluene using a Photovolt integrator Model 49 to compare the peak areas.

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(13) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 330.

Stable Carbocations. CXXII.[1] Diprotonation of Allophanates and Their Cleavage Reactions to Alkylcarbenium Ions and Diprotonated Allophanic Acid in Fluorosulfuric Acid–Antimony Pentafluoride ("Magic Acid"®) Solution

GEORGE A. OLAH,* ALICE T. KU,[2] AND JUDITH A. OLAH

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

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The behavior of alkyl allophanates has been investigated in FSO_3H–SbF_5–SO_2 solution. Carbonyl oxygen diprotonation was observed in all cases by means of low-temperature pmr spectroscopy. With some of the diprotonated allophanates, cleavage occurred in the extremely strong acid system at higher temperatures to give stable alkylcarbenium ions and diprotonated allophanic acid. The elusive allophanic acid thus was directly observed for the first time in its stable diprotonated form.

Protonated amides and alkyl carbamates have been investigated in superacid solutions.[3-6] The protonation of allophanates, their cleavage reactions, and the possibility of the existence of allophanic acid in its diprotonated form have not as yet been investigated. It was felt of interest to extend our studies to the behavior of allophanates in FSO_3H–SbF_5–SO_2 solution and to investigate, over a range of temperature, their cleavage reactions.

Results and Discussion

Methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, and *tert*-butyl allophanates were studied in FSO_3H–

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