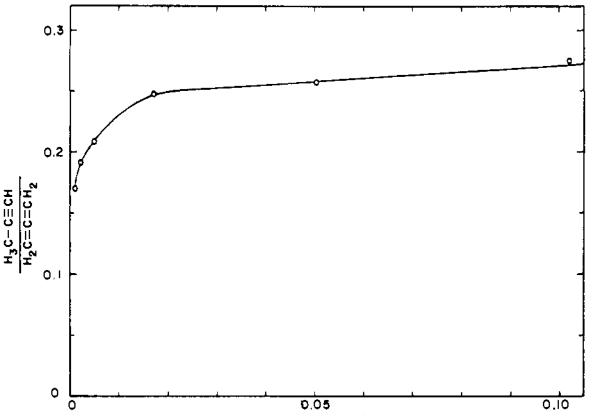
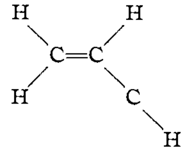


Fig. 3.—The ratio methylacetylene/allene as a function of the reciprocal of the initial total pressure for $C_2H_4/C_3O_2 \geqslant 10$.

When first formed, the C_3H_4 will also have excess energy, partly from the excess remaining on the intermediate, and partly from the energy released in bond formation. Therefore, isomerization is possible, and it is not surprising that at least two C_3H_4 isomers are formed. However, the dependence of the ratio of methylacetylene/allene on the total pressure is not that expected for a simple isomerization of a hot allene molecule to the thermodynamically more stable methylacetylene ($\Delta H_f° = 44.32$ kcal./mole) in competition with collisional stabilization to allene ($\Delta H_f° = 45.92$).[11] The ratio methylacetylene/allene plotted against the reciprocal of the total pressure is not a straight line, as can be seen in Fig. 3 (*cf.* the addition of CH_2 to propene to form hot methylcyclopropane molecules, which can isomerize to butenes or be stabilized by collisions).[12] Measurements up to several atmospheres total pressure will be required to determine whether allene is the exclusive C_3H_4 product in the limit of high pressures. The non-linearity of Fig. 3 might be caused by a multistep deactivation of the hot C_3H_4 molecules, or by a change in the nature of the reactive intermediate.

It is also possible that the two isomers are formed as the result of two different types of attack on the ethylene molecule. Attack on the carbon–carbon double bond could lead, by simple carbon insertion, to allene. Insertion into a carbon–hydrogen bond would give an intermediate of the form



which could rearrange, by the migration of a hydrogen atom, to either of the observed C_3H_4 isomers. However, this mechanism alone cannot explain the observed pressure dependence. Isotopic labeling studies, especially on the methylacetylene, would be useful in establishing the nature of the processes responsible for the two products.[13]

It is a pleasure to thank Professor F. E. Blacet for the loan of equipment and the National Science Foundation for financial assistance. In addition, I wish to thank Professor R. Wolfgang for a prepublication copy of his manuscript.

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(11) F. D. Rossini, *et al.*, "Selected Values of Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44 (1953).

(12) J. N. Butler and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **82**, 759 (1960).

(13) Note Added in Proof.—An isotopic labeling study of the system C_3O_2–C_2H_4 has been published recently (R. T. Mullen and A. P. Wolf, *J. Am. Chem. Soc.*, **84**, 3214 (1962)). The observation of 8% end labeling in the product allene is consistent with some initial C–H bond insertion, although hot molecule isomerization could also be responsible.

[Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Can.]

The Reactions of Sulfur Atoms. I. The Addition to Ethylene and Propylene

By Otto P. Strausz and Harry E. Gunning

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Atomic sulfur, in the (^1D) metastable state, was generated, at 25°, by the *in situ* photolysis of gaseous carbonyl sulfide in the wave length region, 2550–2290 Å. Pure carbonyl sulfide yields CO and sulfur as the main reaction products. On addition of ethylene or propylene to the system, the corresponding cyclic sulfides are formed with a simultaneous decrease in the CO yield. This latter decrease approaches nearly 50% at sufficiently high pressures of added olefin. No major isomerization or cracking of the cyclic sulfide product was observed and its yield varied between 60% and 100% in the experiments. The value of the relative rate constant $k_{C_3H_6}/k_{C_2H_4}$ for the addition reaction was found to be 3.6, while the relative rate constants for the addition to olefin compared to the abstraction reaction from COS were found to be a function of the added olefin pressure. A mechanism is proposed for the reaction, and the roles of S(^1D) and S(^3P) therein are discussed.

Introduction

The renewed interest in atomic reactions in recent years is indicated by the increasingly large number of publications in that field. The success achieved in correlating rate constants to physicochemical properties of substrate molecules has led to a deeper understanding of elementary processes. Despite the progress made, there still exists a large number of reactions which have not yet received sufficient attention. The present investigation is the first in a series of studies to obtain insight into one such type of process, namely, the reactions of sulfur atoms.

Literature data indicated that the photolysis of carbonyl sulfide might be a convenient source of generating sulfur atoms at room temperature. It has been pointed out[1] that the energy available at the onset of the absorption continuum (*ca.* 2550 Å.)

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(1) W. Lochte-Holtgreven, C. E. H. Bawn and E. Eastwood, *Nature*, **129**, 869 (1932).

is just sufficient to rupture the C–S bond and promote $S(^3P)$ to $S(^1D)$

$$\mathrm{COS} + h\nu \longrightarrow \mathrm{CO} + \mathrm{S}(^1\mathrm{D}) \qquad (1)$$

Reaction 1 is also supported by the spin-conservation rule, insofar as it is obeyed in this process, the sulfur atoms being formed in their first excited singlet state. The absorption spectrum of carbonyl sulfide shows two continua.[2] The first one extends down to 1600 Å. where there is a definite break in the absorption. At shorter wave length (~1550 Å.) a new electronic transition appears. A sharp maximum occurs at 2080 Å. and a rounded one at 2250 Å.[3] At these maxima Forbes and Cline[3] found a quantum yield of nearly unity for permanent gas formation (assumed to be carbon monoxide). Kondratjev[4] studied the oxidation of the sulfur produced from COS by photolysis in the presence of O_2. The reaction was monitored by means of the absorption spectrum of SO_2, the main product of the reaction. The mechanism proposed was

$$\mathrm{COS} + h\nu \longrightarrow \mathrm{CO} + \mathrm{S} \qquad (2)$$

$$\mathrm{S} + \mathrm{COS} \longrightarrow \mathrm{CO} + \mathrm{S}_2 \qquad (3)$$

$$\mathrm{S}_2 + \mathrm{O}_2 \longrightarrow \mathrm{SO}_2 + \mathrm{S} \qquad (4)$$

$$\mathrm{S} + \mathrm{SO}_2 \longrightarrow \mathrm{S}_2\mathrm{O}_2 \qquad (5)$$

$$\mathrm{S}_2\mathrm{O}_2 \xrightarrow{\text{Wall}} \mathrm{SO}_2 + \mathrm{S} \qquad (6)$$

A value of 6 kcal./mole was found for the activation energy of step 3, assuming zero activation energy for 5.

Experimental

Conventional high-vacuum techniques were employed throughout the investigation. For the reaction cell a cylindrical quartz tube, 100 mm. in length and 45 mm. in o.d. was used. The radiation source was a Hanovia, model 30620, medium-pressure Hg arc, with a layer of 6 mm. thick Vycor #7910 glass and a neutral density filter interposed between the arc and the cell. The light entering the reaction cell was roughly collimated by means of two 45-mm. apertures, 30 mm. apart. The short wave length limit was 2290 Å. while the long wave length limit was fixed by the absorption spectrum of COS, which starts to absorb at 2550 Å.[1] Reactions were carried out at room temperature. Exposure time varied from 6 to about 300 minutes. CO was measured in a capillary gas buret with correction by mass spectrometric analysis for C_2H_4 carried over with the CO. The excess reactants, COS and C_2H_4 or COS and C_3H_6, were distilled off at −130°, while C_2H_4S and C_3H_6S, which are involatile at this temperature, were retained in the trap. The sulfide products were measured in the gas buret and analyzed by mass spectrometry. Their identification was made by comparison of their mass spectra and infrared spectra with those of authentic samples. The latter were prepared by the method of Searles and Lutz[5] and purified by preparative gas liquid chromatography on a tricresyl phosphate column at 80°. Carbonyl sulfide (Matheson), ethylene and propylene (Phillips Research Grade, 99.98%) were thoroughly degassed and bulb-to-bulb distilled *in vacuo* several times. Since some oxygen-containing impurity (peroxide or hydroperoxide) was retained even after the most careful distillation, the reaction mixtures were further purified by pre-irradiation. This effect is illustrated by the mass spectral data in Table I which were obtained for a mixture of 210 mm. of COS and 50 mm. of C_2H_4. The 59 peak in the table arises from C_2H_4S ($C_2H_3S^+$) and the 64 peak from SO_2 (SO_2^+). After a few tenths of a per cent. of substrate conversion, SO_2 disappears from the condensable products and the only compound remaining is C_2H_4S. When SO_2 is formed, the CO yield values are erratic and the apparent rates of CO and C_2H_4S formation are reduced.

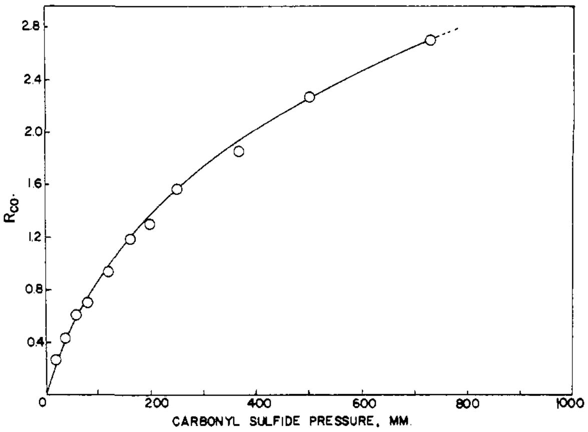

Fig. 1.—The rate of CO formation, in μmoles/30 min., as a function of the pressure of carbonyl sulfide for the wave length region 2290–2550 Å.

TABLE I

REMOVAL OF SO_2-FORMING IMPURITIES BY SUCCESSIVE PRE-IRRADIATION FOR A MIXTURE OF 210 MM. OF COS AND 50 MM. OF C_2H_4

Run	Condensable yield, μmoles	Ratio of peak heights[a] mass 59/mass 64
1	1.36	0.56
2	0.80	0.72
3	1.14	4.44
4	0.56	22.3

[a] The ratio of mass 59 to mass 64 shows the relative yields of C_2H_4S to SO_2.

Results and Discussion

When pure COS is exposed to radiation in the wave length region 2290–2550 Å., the only major gaseous product is CO. In a typical run, with P_{COS} = 105.5 mm., 22.51 μmoles of CO was formed in 60 min. of irradiation. Condensable products at −130° amounted to 0.09 μmole (mainly SO_2 and CS_2), or *ca.* 0.4% of the CO formed.

In Fig. 1 the rate of CO formation, R_{CO} in μ moles/30 min., is shown as a function of $P_{(\mathrm{COS})}$. In these runs the reaction time was progressively reduced with increasing P_{COS} in order to keep the amount of sulfur deposited constant. Conversions were <0.1%. The graph shows no evidence of collisional deactivation; therefore the existence of an excited molecule mechanism can be discounted.

Figure 2 shows the amount of CO formed in μ moles as a function of reaction time for P_{COS} = 202 mm. in the range of 0.6–2.2 μmoles, where most of the runs fell. The nearly linear relation between exposure time and the amount of CO formed indicates no serious interference from either sulfur deposition on the face of the reaction vessel or from any possible recombination processes in this range of conversion.

When ethylene was added to the COS, ethylene sulfide (thiacyclopropane), $\underset{\diagdown\;\diagup}{\mathrm{CH_2{-}CH_2}}$ over S, and with added propylene, propylene sulfide (methyl thia-

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[2] W. C. Price and D. M. Simpson, *Proc. Roy. Soc.* (*London*), **A169**, 501 (1939).

[3] G. S. Forbes and J. E. Cline, *J. Am. Chem. Soc.*, **61**, 151 (1939).

[4] V. Kondratjev, *Acta Physicochim. U.R.S.S.*, **16**, 272 (1942).

[5] S. Searles and E. F. Lutz, *J. Am. Chem. Soc.*, **80**, 3168 (1958).

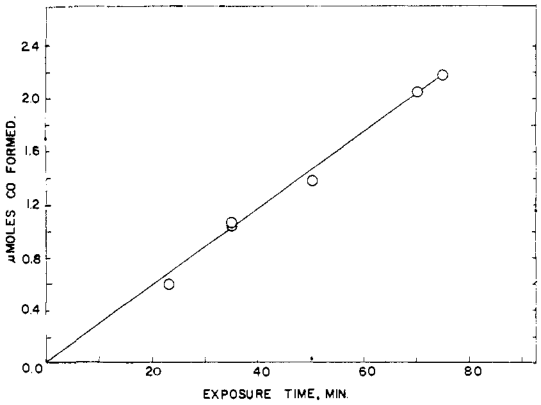


Fig. 2.—The rate of CO formation in μmoles, as a function of exposure time at 202.4 mm. COS pressure.

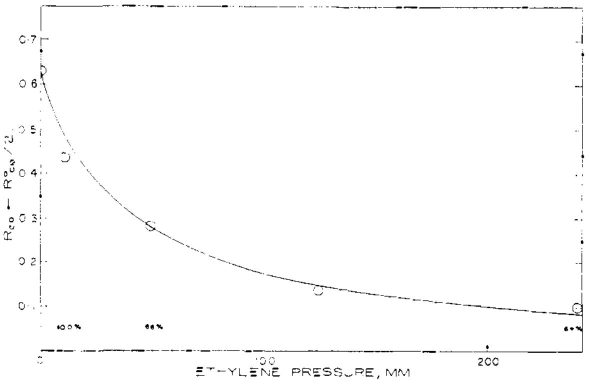
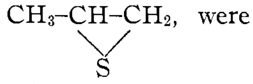


Fig. 3.—The variation of $R_{CO} - R_{CO}^0/2$, the rate of S. formation, as a function of added ethylene, for a constant COS pressure of 200 mm. The solid line represents the calculated curve for $k_7/k_3 = 5.15$. The percentages shown represent the percentage of the theoretical yields obtained for ethylene sulfide.

cyclopropane),  $CH_3\text{–}CH\text{–}CH_2$ (S bridging), were formed, accompanied by a simultaneous decrease in the CO yield. The sulfide yield varied from 60 to 100% in the experiments, as based on the CO yield decrease. The maximum decrease, about 43%, occurred at the highest added propylene pressure—392 mm. A simple mechanism which would account for these observations to a first approximation is

$$COS + h\nu \longrightarrow CO + S \qquad (2)$$

$$S + COS \longrightarrow CO + S_2 \qquad (3)$$

$$S + \text{olefin} \longrightarrow \text{sulfide} \qquad (7)$$

$$nS_2 \longrightarrow S_{2n} \qquad (8)$$

A steady-state treatment yields the following expression for R_{S_2}—the rate of abstraction as a function of olefin pressure at constant P_{COS}

$$R_{S_2} = R_{CO} - R_{CO}^0/2 = \frac{k'}{P_{\text{olefin}} + k}$$

where

R_{CO} = rate of CO formation
R_{CO}^0 = rate of CO formation at $P_{\text{olefin}} = 0$
$k = k_3P_{COS}/k_7$ and $k' = kR_{CO}^0/2$

The experimental points shown in Fig. 3 for C_2H_4 and in Fig. 4 for C_3H_6 were obtained at P_{COS} = 200 mm. The curves were calculated from the above formula, using the mean of the experimental k_7/k_3 values, which were 5.15 for C_2H_4 and 9.39 for C_3H_6. However, the actual mechanism appears to be more complex. This is indicated by the similar gradual decrease in the k_7/k_3 ratios with increasing olefin pressure for both C_2H_4 and C_3H_6 as seen in Table II. However, the ratio of propylene to ethylene, which gives the relative rate of the addition reaction at any corresponding pressure, seems to be constant and equal to nearly 2. This relative rate constant was also determined by an independent technique, the results of which are presented in Table III and Fig. 5. In these experiments a mixture consisting of 50 mm. of COS, 100 mm. of C_2H_4 and 100 mm. of C_3H_6 was irradiated for various periods of time and the relative rates were obtained from the ratio of C_3H_6S to C_2H_4S in the products as determined by mass spectrometry. This ratio was found to be slightly dependent on the exposure time. A linear extrapolation to zero exposure time gave a value for $k_{(C_3H_6 + S)}/k_{(C_2H_4 + S)} = 3.6$ (Fig. 5). Since this competitive technique appears to yield results which are less dependent on any complexity in the reaction mechanism, this value of 3.6 is regarded as the correct one. In Table IV, a comparison is given for the relative addition rate of various reac-

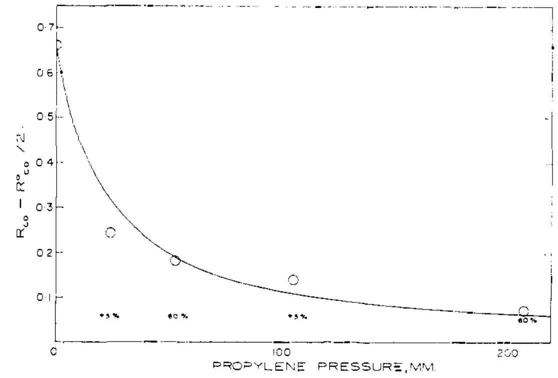


Fig. 4.—The variation of $R_{CO} - R_{CO}^0/2$, the rate of S_2 formation as a function of the added propylene pressure, for a constant COS pressure at 200 mm. The solid line represents the calculated curve for $k_7/k_3 = 9.39$. The percentages shown on the graph indicate the percentage of the theoretical yields of propylene sulfide actually obtained.

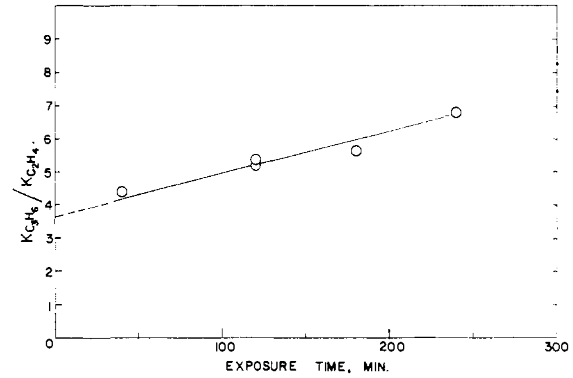


Fig. 5.—The dependence of $k(C_3H_6 + S)/k(C_2H_4 + S)$ on the exposure time.

tants to C_3H_6 and C_2H_4. It is obvious that the sulfur atom behaves like an electrophilic reagent in these reactions, but its electrophilic character is somewhat less marked than that of the oxygen atoms, as might be expected. One striking difference, however, between O and S atom addition is that in the latter there is no major isomerization or cracking, even when the substrate is ethylene. The lower-than-100% yield at least partly can be explained by mechanical loss and by some secondary reactions, such as polymerization, photodecomposition, reaction with sulfur atom, etc. The heat of formation of C_2H_4S is 19.3 kcal./mole,[6] while that for C_2H_4 and S are 12.5 and 53.3 kcal./mole, respectively.[7] Thus the enthalpy decrease for the addition reaction is about 46.5 kcal./mole, if the S atom is in the ground (^3P) electronic state.

TABLE II

APPARENT k_7/k_3 VALUES AS A FUNCTION OF OLEFIN PRESSURE FOR P_{COS} = 200 MM.

$P_{C_2H_4}$, mm.	k_7/k_3	$P_{C_3H_6}$, mm.	k_7/k_3
11.45	7.52	24.00	13.81
50.10	4.88	53.30	9.18
125.1	3.88	106.0	7.00
240.9	4.38	208.0	7.57
392.6	1.52	392.8	3.15

TABLE III

THE CALCULATED RELATIVE RATE CONSTANTS FOR THE ADDITION OF S ATOMS TO PROPYLENE AND ETHYLENE AS A FUNCTION OF DURATION OF EXPOSURE

Run	Exp. time, min.	$P_{C_3H_6}$, mm.	$P_{C_2H_4}$, mm.	CO, μmoles	Condensable, μmoles	Yield of sulfide, %	$\frac{k_{C_3H_6}}{k_{C_2H_4}}$
1	120	100.46	99.64	0.912	0.567	..	5.21
2	180	100.44	99.63	1.35	.703	52	5.65
3	240	100.39	99.60	1.68	.982	58	6.89
4	120	100.33	99.58	0.721	.359	50	5.33
5	40	100.30	99.57	0.231	.122	52	4.46

TABLE IV

RELATIVE RATES OF ADDITION OF REACTANTS TO PROPYLENE AND ETHYLENE

Addend	$k(C_3H_6)/k(C_2H_4)$	Ref.
O	6.1	a
O_3	2.3-2.8	b, d
Br_2	2.0	c
S	3.6	

[a] R. F. Cvetanovic, *J. Chem. Phys.*, **30**, 19 (1959). [b] R. D. Cadle and C. Schadt, *J. Am. Chem. Soc.*, **74**, 6002 (1952). [c] S. V. Anantakrishnan and C. K. Ingold, *J. Chem. Soc.*, 1396 (1935). [d] R. F. Cvetanovic, *Can. J. Chem.*, **38**, 1053 (1960).

Presumably the energy-rich triplet biradical could re-form the cyclic sulfide by collisional deactivation. To this point, we have so far neglected the possible electronic excitation of the sulfur atom in the primary step. It was stated above that both the energetics of the photolysis of COS and the spin-conservation rule would suggest that the initially-formed S atoms should be in the (^1D) metastable state. Indeed, our observation on the pressure dependence of the k_7/k_3 values strongly supports the primary formation of excited S atoms. The following mechanism is proposed to account for the participation of S(^1D) and S(^3P) in the reaction

$$\mathrm{COS} + h\nu \longrightarrow \mathrm{CO} + \mathrm{S}(^1D) \quad (1)$$

$$\mathrm{S}(^1D) + \mathrm{COS} \longrightarrow \mathrm{CO} + \mathrm{S_2} \quad (9)$$

$$\mathrm{S}(^1D) + \mathrm{C_2H_4} \longrightarrow \mathrm{C_2H_4S}^* \quad (10)$$

$$\mathrm{S}(^1D) + \mathrm{C_2H_4} \longrightarrow \mathrm{C_2H_4}^* + \mathrm{S}(^3P) \quad (11)$$

$$\mathrm{S}(^3P) + \mathrm{C_2H_4} \longrightarrow \mathrm{C_2H_4S} \quad (12)$$

$$\mathrm{S}(^3P) + \mathrm{COS} \longrightarrow \mathrm{CO} + \mathrm{S_2} \quad (13)$$

$$n\mathrm{S_2} \longrightarrow \mathrm{S_{2n}} \quad (8)$$

The steady-state calculation on this mechanism shows that

$$R_{S_2} = \frac{R_{CO}^0}{2}\,\frac{A + BP}{A + CP + DP^2}$$

where

$A = k_9 k_{13} P^2{}_{COS}$

$B = [k_9 k_{12} + k_{11} k_{13}] P_{COS}$

$C = [k_9 k_{12} + (k_{10} + k_{11}) k_{13}] P_{COS}$

$D = (k_{10} + k_{11}) k_{12}$

and P is the olefin pressure.

The graph of this function is in qualitative agreement with the shape of the experimental curve. Now, if k_{13} is equal to zero, this expression becomes equivalent to the previous one and k_7/k_3 should be constant. In order to obtain the experimentally-observed effect, k_9 has to be greater than k_{13}, which is a reasonable assumption, since the ^1D metastable state lies 26.4 kcal. above the ground state. It also follows from the mechanism that olefins are more efficient in deactivating S(^1D) atoms to the ground state than COS, and this would explain why the relative addition rates obtained by the two methods differ. It also must be emphasized that both S(^1D) and S(^3P) addition are occurring simultaneously and likely with different rate constants. Therefore the value of 3.6 for the relative rate constant must be regarded as a mean value for the particular concentration ratio of S(^1D) to S(^3P) obtaining in the present system. By further studies now in progress in this Laboratory on the reactions of sulfur atoms with olefins and paraffins, it is hoped to obtain further insight into the kinetics of this interesting group of reactions.

Acknowledgments.—The authors would like to express their deep appreciation to Mr. Gene Fried for valuable assistance in the experimental work, and to Mr. R. K. Taylor for the mass spectrometric analysis. This work was partially supported by a grant from Imperial Oil Limited, which support is gratefully acknowledged.

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[6] G. B. Guthrie, D. W. Scott and Guy Waddington, *J. Am. Chem. Soc.*, **74**, 2795 (1952).

[7] "Selected Values of Chemical Thermodynamic Properties," Circular of the National Bureau of Standards, 1952.