Obviously a firm conclusion as to the detailed mechanism of the $^3SO_2$–RH reactions is not possible from the data at hand. However, the present data and the results of all previous studies seem most consistent with the H-abstraction mechanism, reaction 9a''. We are undertaking more detailed product rate studies of SO_2–RH systems to help delineate the details of these most interesting reactions.

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Mechanism of the Photolysis of Mixtures of Sulfur Dioxide with Olefin and Aromatic Hydrocarbons

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Abstract: Triplet sulfur dioxide molecules ($^3SO_2$) were excited directly by absorption of a laser pulse of 3828.8-Å light within the "forbidden" $SO_2(^1A_1) \rightarrow SO_2(^3B_1)$ band. From the measured phosphorescence intensities as a function of time, the $^3SO_2$ lifetimes were determined in experiments at 25° and at varied pressure of added olefinic or aromatic hydrocarbon or ketone. The slopes of the plots of $1/\tau$ *vs.* added reactant pressure gave the following $^3SO_2$ quenching rate constant estimates (l./(mol sec) $\times 10^{-10}$): ethylene, 4.16 ± 0.50; trichloroethylene, 2.25 ± 0.21; trifluoroethylene, 1.06 ± 0.07; propylene, 8.50 ± 0.87; *cis*-2-butene, 13.40 ± 0.98; cyclopentene, 10.5 ± 1.7; benzene, 8.13 ± 0.68; hexafluorobenzene, 0.869 ± 0.093; acetone, 0.119 ± 0.011; and biacetyl, 14.2 ± 1.0. These rate constant data and a $^3SO_2$ reaction mechanism are shown to be consistent with the previously published product rate studies of SO_2–olefin systems photolyzed within the first allowed SO_2 absorption band (2400–3200 Å). It is concluded that the photochemical changes in all of these systems result from the reactions of the $^3SO_2$ molecules alone. The singlet excited state of SO_2 seems important only as a source of $^3SO_2$ molecules through intersystem crossing. Speculation is given concerning the detailed mechanism for $^3SO_2$ quenching reactions in the SO_2–olefin mixtures. All of the published data fit well the hypothesis that the quenching reactions involve a strong interaction between the π-electron system of the olefin and the electrophilic reagent $^3SO_2$. This interaction is presumed to lead ultimately to the addition of $^3SO_2$ to the double bond. The several overall photochemical processes which have been observed in these systems can be rationalized well in terms of four alternative reaction paths of the intermediate diradical product formed in the addition reaction.

There has been an increased interest in the mechanisms of the thermal and the photochemical reactions of sulfur dioxide. The evaluation of the extent of the participation of the two emitting states, the first excited singlet ($^1SO_2$) and the lowest triplet state ($^3SO_2$), in the photochemistry of sulfur dioxide has attracted considerable academic attention. Interest has been stimulated by the practical concern over the nature and the mechanism of the SO_2 removal paths in urban atmospheres. The possible role of SO_2 in aerosol formation in olefin-containing, auto-exhaust-polluted environments has been suggested.[1–5]

Several quantitative studies have been made of the reactions of the photoexcited sulfur dioxide with olefins in which the excitation of the SO_2 was effected within its first allowed absorption band (2400–3200 Å). The first study was by Dainton and Ivin.[6] They found that sulfinic acid products of unidentified structures were formed in SO_2–olefin mixtures irradiated with the full Hg arc. In a single experiment using a 1-butene–SO_2 mixture, they found that one molecule of SO_2 disappeared per molecule of the olefin which reacted. The quantum yield of sulfinic acid formation in equimolar olefin–SO_2 mixtures varied with the olefin structure: 0.013 for ethylene, 0.020 for propylene, 0.044 for 1-butene, and 0.033 for 2-butene. A series of detailed kinetic studies with 1-butene–SO_2 mixtures gave results which Dainton and Ivin found to be impossible to rationalize quantitatively. They observed that the addition of small quantities of 1-butene inhibited the formation of sulfinic acid in the photolysis of SO_2–*n*-butane mixtures. They reasoned that the inhibition resulted from the strong quenching of the olefin. However, an attempted kinetic treatment of the data gave the impos-

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(1) E. A. Shuck, H. W. Ford, and E. R. Stephens, Report No. 26, Air Pollution Foundation, San Marino, Calif., Oct 1958.

(2) E. R. Stephens and E. A. Schuck, *Chem. Eng. Progr.*, **54**, 71 (1958).

(3) N. A. Renzetti and G. J. Doyle, *J. Air Pollut. Contr. Ass.*, **8**, 293 (1959).

(4) N. A. Renzetti and G. J. Doyle, *Int. J. Air Pollut.*, 327 (1959).

(5) H. S. Johnston and K. Dev Jain, *Science*, 131, 1523 (1960).

(6) (a) F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.*, **46**, 374 (1950); (b) *ibid.*, **46**, 382 (1950).

sible result that the ratio of the quenching ability of *n*-butane to that for 1-butene was equal to 2.8. Hence, they could ascribe no physical meaning to their empirical kinetic expressions which fit the experimental results.

In their studies of the polysulfone formation through the copolymerization of SO_2 and 2-butene, Bristow and Dainton[7a] first observed that irradiated mixtures of pure *cis*- or *trans*-2-butene in liquid SO_2 resulted in a rapid cis–trans isomerization in addition to the polymerization reaction. The experiments showed a large "skin" effect and variable induction periods which prevented a quantitative study of the photochemical system. Cundall and Palmer[7b] found similar results in a brief study of the gas-phase SO_2-photosensitized reaction of *cis*-butene and 1-butene. *cis*-2-Butene–SO_2 mixtures were irradiated with the full Hg arc in runs of 5–41-hr duration. They found that in addition to sulfinic acid formation, a cis–trans isomerization occurred and a less efficient production of 1-butene. 1-Butene–SO_2 mixtures also formed small amounts of 2-butene isomer after prolonged irradiation. They interpreted the cis–trans isomerization result in terms of a triplet energy-transfer reaction from excited SO_2 to olefin. The double-bond-switching reaction was thought to result from excited SO_2 addition to the double bond followed by a mechanistically unspecified rearrangement.

Recently Cehelnik, Spicer, and Heicklen[8] studied the reaction of photoexcited SO_2 (3130 Å) with C_2F_4. In this system CF_2O was observed as the major product. Its quantum yields were small and nearly constant (0.05 ± 0.02) for all runs at varied SO_2 and C_2F_4 pressures. Nitric oxide suppressed the product formation. The authors rationalized their results in terms of two electronically excited states of SO_2 which are different from those which fluoresce and phosphoresce.

Recent studies from our laboratory have shown convincingly that the sulfur dioxide triplet phosphorescent state is largely, if not solely, responsible for the photochemical changes which occur in pure SO_2,[9,10] SO_2–CO mixtures,[11] and in SO_2–paraffin hydrocarbon mixtures.[12] This appears to be the case for SO_2 excited within either the first allowed or the singlet–triplet absorption regions. In the most recent of these studies we have utilized a 3828.8-Å laser source to excite $^3SO_2$ species directly by light absorption within the "forbidden" $SO_2(^1A_1) \rightarrow SO_2(^3B_1)$ band. In this fashion we have avoided the very extensive kinetic complications encountered in attempted quantitative studies of SO_2 triplet molecules formed by way of intersystem crossing.

In the work which we describe here the 3828.8-Å laser technique has been employed to study the lifetimes of $^3SO_2$ in mixtures with a variety of olefin and aromatic hydrocarbons. The results allow a quantitative evaluation of the $^3SO_2$ quenching rate constants for these compounds. The rate constant data, coupled with the results of some of our previous studies, allow a realistic interpretation of the previous SO_2–olefin studies in which SO_2 was excited by way of the singlet species.

Table I. The Inverse Lifetimes of Sulfur Dioxide Triplet Molecules in Mixtures of Sulfur Dioxide (1.55 Torr) with Various Olefin and Aromatic Hydrocarbons at 25°

P_{RH}, Torr × 10^3	$1/\tau$, sec^{-1} × 10^{-4}
(a) Ethylene	
0.0	4.01
4.3	5.29
6.4	5.87
8.1	5.91
9.1	6.24
10.7	6.32
12.5	7.81
14.6	7.29
16.0	7.50
17.8	7.93
21.6	9.27
25.0	9.81
(b) Trichloroethylene	
0.0	3.99
9.7	5.77
17.3	6.86
26.7	7.73
34.9	9.23
42.7	9.72
47.3	10.6
52.3	11.4
66.1	11.9
75.6	13.7
(c) Trifluoroethylene	
0.0	3.90
10.4	4.41
29.9	5.84
52.3	6.80
81.1	8.12
101	9.66
113	10.2
131	11.9
150	12.2
(d) Propylene	
0.00	4.25
0.98	4.66
1.7	5.15
2.6	5.61
3.0	5.70
4.7	6.57
6.2	6.95
7.5	8.08
10.1	9.74
11.7	9.33
13.4	10.2
(e) *cis*-2-Butene	
0.0	4.06
2.0	5.73
2.4	6.48
3.1	6.75
4.1	6.99
4.1	7.34
5.0	8.49
6.1	9.10
6.9	9.62
7.5	10.4
8.2	10.3
9.0	10.8
9.4	11.9
10.9	11.6
11.9	12.8
12.7	13.7
(f) Cyclopentene	
0.0	4.03
3.1	6.54
5.3	7.72
8.5	9.67
11.2	11.3
13.9	11.7
(g) Benzene	
0.0	4.09
0.79	4.26
1.4	4.78
2.0	5.04
2.8	5.23
4.0	6.12
5.0	7.14
5.2	6.45
6.5	7.72
7.0	8.15
8.3	8.18
10.3	9.05
11.8	9.20
13.0	9.61
13.3	9.79
14.6	10.6
16.5	11.6
(h) Hexafluorobenzene	
0.0	3.91
10.3	4.45
51.5	5.76
79.5	8.15
122	10.6
152	10.6
190	13.1
242	15.0

Experimental Section

The triplet sulfur dioxide molecules were excited directly by a 20-nsec pulse of 3828.8-Å laser light within the $SO_2(^1A_1) \rightarrow SO_2(^3B_1)$ "forbidden" band of SO_2. The details of the laser system and the equipment for the phosphorescence lifetime measurements have been given previously and need not be repeated here.[13] In the experiments with biacetyl a Corning C.S.7-59 filter was placed in front of the photomultiplier to remove biacetyl phosphorescence. The reactant hydrocarbons employed were the high-purity products

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(7) (a) G. M. Bristow and F. S. Dainton, *Proc. Roy. Soc., Ser. A*, 229, 525 (1955); (b) R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, **56**, 1211 (1960).

(8) E. Cehelnik, C. W. Spicer, and J. Heicklen, *J. Amer. Chem. Soc.*, submitted for publication; private communication to the authors.

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(10) T. N. Rao, S. S. Collier, and J. G. Calvert, *J. Amer. Chem. Soc.*, **91**, 1609 (1969).

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(12) C. C. Badcock, H. W. Sidebottom, J. G. Calvert, G. W. Reinhardt, and E. K. Damon, *ibid.*, **93**, 3115 (1971).

(13) H. W. Sidebottom, C. C. Badcock, J. G. Calvert, G. W. Reinhardt, B. R. Rabe, and E. K. Damon, *ibid.*, **93**, 2587 (1971).

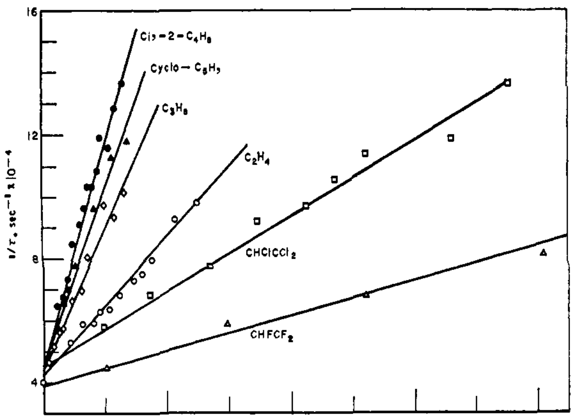

Figure 1. Stern–Volmer plots of the reciprocal lifetimes of $^3SO_2$ *vs.* the pressure of added olefinic hydrocarbon obtained from SO_2–hydrocarbon mixtures at 25° and $P_{SO_2} = 1.55$ Torr; $^3SO_2$ molecules were excited directly in these experiments using a 3828.8-Å laser pulse.

of the Phillips Petroleum Co. or the Matheson Chemical Co. The sulfur dioxide was the anhydrous product of Matheson. The biacetyl was the Fluka product (puriss) (Columbia Chemical Co.). Each of the compounds was further purified by bulb-to-bulb distillation in the high-vacuum line in which it was stored. The biacetyl was purified by discarding a light fraction distilling at the temperature of a $CHCl_3$ melt (−63°), collecting a center fraction distilling from a CCl_4 melt (−23°), and discarding the residue. Acetone was the reagent grade product of the J. T. Baker Chemical Co.

The gaseous mixtures were prepared in a mercury-free system using a Pyrex spiral manometer as a null instrument for measurements of pressure. A thermal gradient pump in series with the cell was used to mix the reactants.

The measured lifetimes of $^3SO_2$ in SO_2 mixtures with various olefin and aromatic hydrocarbons are given in Table I. Those from SO_2 mixtures with biacetyl and acetone are shown in Table II.

Table II. The Inverse Lifetimes of Sulfur Dioxide Triplet Molecules in Mixtures of Sulfur Dioxide (1.55 Torr) with Acetone and Biacetyl at 25°

Pressure of Me_2CO, Torr	$1/\tau$, $sec^{-1} \times 10^{-4}$	Pressure of Ac_2, Torr $\times 10^3$	$1/\tau$, $sec^{-1} \times 10^{-4}$
0.000	4.12	0.00	3.94
0.099	4.51	1.94	5.88
0.190	5.68	3.10	6.63
0.298	6.53	5.15	8.28
0.495	7.63	7.21	9.02
0.640	8.88	8.30	10.2
0.792	10.2	10.0	11.0
0.964	9.74	11.7	13.2
1.15	12.0	12.9	14.2
1.28	12.0	14.0	15.1
1.49	14.0		

A measure of the degree of reproducibility of the measured lifetimes is had from a comparison of the values found in the repeated determinations in pure SO_2 at 1.55 Torr made at the start of each of the ten different reactant series. The values are very similar; the average, $1/\tau = (4.03 \pm 0.21) \times 10^4$ sec^{-1}, is in excellent agreement with the value, $1/\tau = (3.97 \pm 0.54) \times 10^4$ sec^{-1}, calculated for a pressure of 1.55 Torr of SO_2 from the least-squares equation of Sidebottom, *et al.*,[13] obtained from measurements in pure SO_2 over a wide range of pressures (0.16–17.6 Torr). Note also the values of the least-squares intercepts of the Stern-Volmer plots summarized in Table III. The data were not forced to pass through the measured values with pure SO_2. The near constancy of these estimates is gratifying and reflects the general consistency of the experimental methods employed.

Discussion

The Determination of the $^3SO_2$ Quenching Rate Constants for the Olefinic and Aromatic Hydrocarbons.

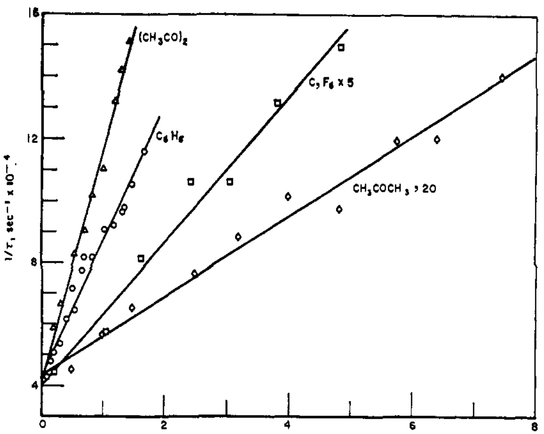

Figure 2. Stern–Volmer plots of the reciprocal lifetimes of $^3SO_2$ *vs.* the pressure of added aromatic hydrocarbon or ketone obtained from SO_2–added gas mixtures at 26° and $P_{SO_2} = 1.55$ Torr; excitation of the $^3SO_2$ molecules was accomplished using a 3828.8-Å laser pulse; the pressures of C_6F_6 and CH_3COCH_3 which were used are given by the number for the abscissa × 5 and × 20, respectively.

The reactions of the excited sulfur dioxide singlet ($^1SO_2$) and triplet molecules ($^3SO_2$) are described well by an extension of the previously proposed reaction mechanism.[10,14]

$$SO_2 + h\nu\ (2400\text{–}3200\ \text{Å}) \longrightarrow {}^1SO_2 \qquad \text{(I)}$$

$$SO_2 + h\nu\ (3390\text{–}3880\ \text{Å}) \longrightarrow {}^3SO_2 \qquad \text{(II)}$$

$${}^1SO_2 + SO_2 \longrightarrow 2SO_2 \qquad \text{(1a)}$$

$$\longrightarrow {}^3SO_2 + SO_2 \qquad \text{(2a)}$$

$${}^1SO_2 + RH \longrightarrow (\text{products or } SO_2 + RH) \qquad \text{(1b)}$$

$$\longrightarrow {}^3SO_2 + RH \qquad \text{(2b)}$$

$${}^1SO_2 \longrightarrow SO_2 + h\nu_f \qquad \text{(3)}$$

$$\longrightarrow SO_2 \qquad \text{(4)}$$

$$\longrightarrow {}^3SO_2 \qquad \text{(5)}$$

$${}^3SO_2 \longrightarrow SO_2 + h\nu_p \qquad \text{(6)}$$

$$\longrightarrow SO_2 \qquad \text{(7)}$$

$${}^3SO_2 + SO_2 \longrightarrow SO_3 + SO \qquad \text{(8a)}$$

$$\longrightarrow 2SO_2 \qquad \text{(8b)}$$

$${}^3SO_2 + RH \longrightarrow (RSO_2H \text{ and other products}) \qquad \text{(9a)}$$

$$\longrightarrow SO_2 + RH \qquad \text{(9b)}$$

RH represents the added olefinic or aromatic hydrocarbon quenching gas. In the quantitative evaluation of SO_2–reactant mixture photolyses within the first allowed absorption band (2400–3200 Å), one must consider all of the reactions I, 1a–9b. The situation is much simplified in the treatment of our present results. The excitation of $^3SO_2$ molecules was effected directly in primary process II by the absorption of a pulse of light at 3828.8 Å. Only reactions 6–9b are required for these conditions, and the lifetime of the triplet species should be given by relation A.

$$1/\tau = k_6 + k_7 + (k_{8a} + k_{8b})[SO_2] + (k_{9a} + k_{9b})[RH] \qquad \text{(A)}$$

The $^3SO_2$ lifetimes were observed in this work in experiments at a fixed pressure of SO_2 and at varied hydrocarbon pressures. The data summarized in Table I fit well the form of relation A. (See the plots of $1/\tau$ *vs.* pressure of hydrocarbon in Figures 1 and 2.) The

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(14) S. S. Collier, A. Morikawa, D. H. Slater, J. G. Calvert, G. Reinhardt, and E. K. Damon, *J. Amer. Chem. Soc.*, **92**, 217 (1970).

Table III. Summary of the Quenching Rate Constant Data for Sulfur Dioxide Triplet Molecules with Various Olefin and Aromatic Hydrocarbons and Ketones at 25°

Compound	Parameters of Stern-Volmer Plots[a]		
	Intercept, $sec^{-1} \times 10^{-4}$	Slope, $(mm\ sec)^{-1} \times 10^{-4}$	k_9, l./(mol sec) $\times 10^{-10}$
Ethylene	4.20 ± 0.38	224 ± 27	4.16 ± 0.50
Trichloroethylene	4.54 ± 0.49	122 ± 11	2.25 ± 0.21
Trifluoroethylene	3.88 ± 0.36	57 ± 4	1.06 ± 0.07
Propylene	4.35 ± 0.33	458 ± 47	8.50 ± 0.87
cis-2-Butene	4.46 ± 0.39	724 ± 53	13.4 ± 0.98
Cyclopentene	4.54 ± 0.75	565 ± 89	10.5 ± 1.7
Benzene	4.31 ± 0.32	438 ± 36	8.13 ± 0.68
Hexafluorobenzene	3.99 ± 0.66	46.8 ± 5.0	0.869 ± 0.093
Acetone	4.35 ± 0.51	6.41 ± 0.60	0.119 ± 0.011
Biacetyl	4.05 ± 0.49	766 ± 56	14.2 ± 1.0

[a] Derived from the least-squares treatment of the $1/\tau$ *vs.* pressure of added quencher gas plots from the data of Tables I and II and Figures 1 and 2; the error limits reported represent the 95% confidence limits (twice the standard deviation).

Table IV. Comparison of the Rate Constants for the Triplet Quenching Reactions of $^3SO_2$, Hg($^3P_1$), and $^3Me_2CO$ by Unsaturated Hydrocarbons and by Ketones and Those for Free Radical Addition to These Compounds at 25°

Compound	Rate constants, l./(mol sec) × factor shown					
	$^3SO_2 \times 10^{-11}$	Hg($^3P_1$)[a] $\times 10^{-11}$	$^3Me_2CO$[d] $\times 10^{-6}$	O(^3P)[e] $\times 10^{-9}$	$H \times 10^{-8}$	$CH_3 \times 10^{-3}$
Ethylene	0.42	3.0	0.53	0.17	5.5[g]	1.3[i]
Propylene	0.85	3.4	1.1	1.1	4.7[h]	1.2[i]
Cyclopentene	1.05			5.5		
cis-2-Butene	1.34	4.0	3.3	3.8	1.4[h]	0.28[i]
Trichloroethylene	0.23	4.0				
Trifluoroethylene	0.11	0.66[b]				5.8[b,j]
Benzene	0.81	2.5[c]	<0.05	<0.02[f]	0.18[h]	
Hexafluorobenzene	0.087					
Acetone	0.012	3.9				
Biacetyl	1.42		2.2×10^4 [k]			

[a] B. DeB. Darwent, M. K. Phibbs, and F. G. Hurtubise, *J. Chem. Phys.*, **22,** 859 (1954). [b] Data for C_2F_4. [c] G. J. Mains and M. Trachtman, *J. Phys. Chem.*, **74,** 1647 (1970). [d] R. E. Rebbert and P. Ausloos, *J. Amer. Chem. Soc.*, **87,** 5569 (1965); calculated from the data they present assuming a collision number of 2×10^{11} l./(mol sec) for each of the cases. [e] R. J. Cvetanović, *J. Chem. Phys.*, **30,** 19 (1959). [f] G. Boocock and R. J. Cvetanović, *Can. J. Chem.*, **39,** 2436 (1961). [g] J. A. Eyre, T. Hikada, and L. M. Dorfman, *J. Chem. Phys.*, **53,** 1281 (1970); high-pressure limit, $P >$ 760 Torr. [h] K. Yang, *J. Phys. Chem.*, **67,** 562 (1963). [i] R. J. Cvetanovic and R. S. Irwin, *J. Chem. Phys.*, **46,** 1694 (1967). [j] J. M. Sangster and J. C. J. Thynne, *Int. J. Chem. Kinet.*, **1,** 571 (1969). [k] J. Heicklen and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **81,** 3858 (1959).

parameters which describe the least-squares lines of the Stern-Volmer plots and the rate constants $k_9 = k_{9a} + k_{9b}$ derived from the slopes are shown in Table III.

There are several observations concerning these rate constants which one can make. (1) The $^3SO_2$ quenching facility of the olefins and aromatics is great indeed. The quenching rate constants are in general about 100 times those for the paraffin hydrocarbons;[12] for *cis*-2-butene the quenching rate constant, 1.3×10^{11} l./(mol sec), is very nearly as large as the collision number, 2.3×10^{11} l./(mol sec). (2) Halogen atom substitution for hydrogen in the olefins lowers the rate constant significantly. The rate constants for the ethylenes decrease in the order $C_2H_4 > C_2Cl_3H > C_2F_3H$. The rate constant for benzene is 9.4 times that for hexafluorobenzene. (3) Increasing the extent of alkyl radical substitution in ethylenes increases the quenching rate constant in the order $C_2H_4 < C_3H_6 <$ c-$C_5H_8 <$ *cis*-2-butene.

In Table IV some insight into the details of the quenching process can be gained by a comparison of the structural effects of the olefinic and aromatic hydrocarbons on the rate constants for $^3SO_2$, Hg($^3P_1$), and $^3Me_2CO$ quenching reactions and the rate constants for addition of some simple atoms and free radicals to these hydrocarbons. Considerable structural selectivity is seen in the $^3SO_2$ quenching reactivity of the olefins. The trend is very similar to that noted by Cvetanovic for O(^3P) and several other electrophilic reactants.[15] It is opposite to that observed for the CH_3 radical addition reactions to olefins. Rousseau, Strausz, and Gunning have noted the similarity in order for the olefin quenching reactions of Hg($^3P_1$) and O(^3P) addition reactions with the olefins, and have concluded that the Hg($^3P_1$) also shows significant electrophilic character.[16] It appears that the $^3SO_2$ may be yet another example of an electrophilic reactant in its quenching reactions with the olefins. The hypothesis seems warranted that the very efficient $^3SO_2$ quenching reaction with the olefins and aromatics is related to the interaction of the electrophilic $^3SO_2$ reactant with the highly polarizable π-electron system of these molecules. Following the Cvetanović picture of O(^3P) atom reactions, the transition state for the quenching interaction may be a highly polarized charge-transfer complex between $^3SO_2$ and the hydrocarbon. The picture is qualitatively in accord with the observed substitutional effects: electron-releasing alkyl-group substitution increases the quenching rate constant, while electron-withdrawing fluorine or chlorine atom substitution lowers the rate constants.

Although the rate-determining step in the Hg($^3P_1$) and $^3SO_2$ quenching reactions with olefins may involve a very similar polar complex between the electrophilic

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(15) (a) R. J. Cvetanovic, *Can. J. Chem.*, **38,** 1678 (1960); (b) R. J. Cvetanović and R. S. Irwin, *J. Chem. Phys.*, **46,** 1702 (1967).

(16) Y. Rousseau, O. P. Strausz, and H. E. Gunning, *ibid.*, **39,** 962 (1963).

molecule and the π system, the subsequent events of the quenching encounters must be quite different. Note in Table IV that the Hg($^3P_1$) quenching rate constants are the largest of those compared and are near the collision number. It is probable that triplet energy transfer accounts for most of the quenching of the Hg($^3P_1$) by olefins.[17] The same mechanism is thought to be operative for triplet acetone quenching by olefins. Rebbert and Ausloos suggested that the significantly lower rates of quenching are the result of the endothermicity of the triplet energy-transfer reactions in this case.[18] While the Hg($^3P_1$) atom is 113 kcal/mol above the Hg($^1S_0$) ground state, the acetone triplet energy level is much lower, probably in the range 77 ± 2 kcal/mol.[19] The SO_2 triplet is 73.7 kcal/mol above the ground state.[20] The triplet energy level for ethylene is somewhat uncertain, but it is probably about 82 kcal/mol;[21] the value is expected to be somewhat less for the olefins with increasing extent of alkyl substitution. However, in the case of $^3Me_2CO$ quenching by biacetyl (E_T = 56 ± 1 kcal/mol),[22] the triplet energy transfer is exothermic and the reaction is near the collision number.

Although the Hg($^3P_1$) and the $^3Me_2CO$ quenching by olefinic hydrocarbons seems to involve a triplet energy transfer, we feel that this mechanism can not be important for $^3SO_2$ quenching by the olefins, contrary to the suggestion of Cundall and Palmer.[7b] The triplet energy of SO_2 must be lower than that of acetone.[19] With the $^3Me_2CO$–olefin reaction, energy transfer is already inefficient, presumably because of the endothermicity of the reaction. Certainly the energy transfer from $^3SO_2$ to the olefins must be much less efficient. There can be no argument that the energy transfer from $^3SO_2$ must be unimportant in the case of benzene as its triplet energy is well established near 84.4 kcal/mol.[20] The reaction of energy transfer will be about 10.7 kcal endothermic in this case. Although only one collision in about 10^8 would have the needed energy deficit for this reaction, benzene quenches $^3SO_2$ at a rate only slightly below the collision number [$k_9 = 0.81 \times 10^{11}$ l./(mol sec)]. Obviously some other mechanism than that of energy transfer must be involved in the $^3SO_2$–olefinic hydrocarbon and $^3SO_2$–aromatic hydrocarbon systems.

The efficient interaction of the $^3SO_2$ with unsaturated bond systems does not extend to the carbonyl double bond. The rate constant for quenching by acetone is much smaller than that of the olefins, about equal to that observed for the saturated hydrocarbon, *n*-butane.[12] Although biacetyl ($E_T \cong 56$ kcal/mol) quenches $^3SO_2$ very efficiently, it is clear that an exothermic triplet energy transfer occurs in this case. From our previous measurements of the quantum yield of the $^3SO_2$-sensitized phosphorescence in biacetyl[23] we can estimate that $k_{9(Ac_2)} = (1.4 \pm 0.7) \times 10^{11}$ l./(mol sec); this is equal within the experimental error to the rate constant estimated here by $^3SO_2$ quenching measurements, $k_{9(Ac_2)} = (1.4 \pm 0.1) \times 10^{11}$ l./(mol sec). It is evident that triplet energy transfer can account quantitatively for the $^3SO_2$ quenching by biacetyl.

Further insight into the detailed mechanism of the $^3SO_2$–olefin reactions can be gathered by considering the previously published photochemical SO_2–olefin product rate studies in which excitation occurred within the first allowed absorption band of SO_2 (2400–3200 Å).

The Mechanism of SO_2–Olefinic Hydrocarbon Reactions Excited at 2400–3200 Å. Recently we have found that the $^3SO_2$ reactions alone were important for product formation in the 2400–3200-Å photolysis of pure SO_2,[9,10] SO_2–CO,[11] and SO_2–paraffin hydrocarbon mixtures.[12] Thus, it is reasonable to attempt to apply the same mechanism to the olefin and aromatic hydrocarbon systems. We will assume as before that the only important reactions of $^1SO_2$ are its deactivation by collision in reaction 1 and its part in forming the reactive $^3SO_2$ molecules in reaction 2. We may accept the ratio of rate constants $k_2/(k_1 + k_2)$ equal to that found for the pure SO_2 system (0.09 ± 0.01).[10,24] Furthermore, the unimolecular reactions of the $^1SO_2$ and $^3SO_2$ species (reactions 3–7) will be unimportant for experiments above 5 Torr.

The first test can be made using the product rate data of Dainton and Ivin determined from the 1-butene-inhibited, full-Hg-arc photolyses of SO_2–*n*-butane equimolar mixtures. In terms of our triplet mechanism relation B should describe the ratio of the rate of the $C_4H_9SO_2H$ formation in the uninhibited photolysis ($R^0{}_{BuSO_2H}$) to that in the inhibited photolyses (R_{BuSO_2H}).

$$\left(\frac{R^0{}_{BuSO_2H}}{R_{BuSO_2H}} - 1\right)[(k_{9a} + k_{9b})_{C_4H_{10}}P_{C_4H_{10}} + (k_{8a} + k_{8b})P_{SO_2}] = (k_{9a} + k_{9b})_{C_4H_8}P_{C_4H_8} \quad \text{(B)}$$

The total sulfinic acid product rates measured by Dainton and Ivin were corrected for the theoretically expected small rate of 1-butenesulfinic acid product to obtain the actual rates of butanesulfinic acid formation used in our treatment.[25] The Dainton and Ivin rate

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(17) R. J. Cvetanović, H. E. Gunning, and E. W. R. Steacie, *J. Chem. Phys.*, **31**, 573 (1959).

(18) R. E. Rebbert and P. Ausloos, *J. Amer. Chem. Soc.*, **87**, 5569 (1965).

(19) An upper limit of 79 kcal/mol can be set for the acetone triplet energy by the position of the 0–0 band of the $S_0 \rightarrow S_1$ transition at 3600 Å [W. A. Noyes, Jr., G. B. Porter, and J. E. Jolley, *Chem. Rev.*, **56**, 49 (1956)]; a lower limit is established from the results of our work. We find that the quenching of $^3SO_2$ by acetone is rather inefficient [$k_9 = 1.2 \times 10^9$ l./(mol sec)], yet SO_2 quenches the acetone triplet at a rate near the collision number: J. W. Gall, D. H. Slater, and J. G. Calvert in "Chemical Reactions in the Urban Atmosphere," C. Tuesday, Ed., American Elsevier, New York, N. Y., in press]. Obviously the triplet of acetone lies somewhat above 73.7 kcal/mol. If the rate of quenching of $^3SO_2$ by acetone is due to energy transfer entirely and the relative slowness results from the endothermicity of the reaction, then we can place the triplet of acetone at about 77 kcal/mol.

(20) G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966, p 588.

(21) E. F. Evans, *J. Chem. Soc.*, 1351 (1957); 1735 (1960).

(22) (a) G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, **66**, 2100 (1944); (b) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).

(23) This was estimated from the measured ratio $(k_{8a} + k_{8b})/k_{9(Ac_2)} = (2.7 \pm 1.4) \times 10^{-3}$ from ref 10, and the most recent value for $k_{8a} + k_{8b} = (3.9 \pm 0.1) \times 10^8$ l./(mol sec) from ref 13.

(24) T. N. Rao and J. G. Calvert, *J. Phys. Chem.*, **74**, 681 (1970).

(25) The Dainton and Ivin data give the measured quantum yields of sulfinic acid formation for equimolar hydrocarbon–SO_2 mixtures to be 0.23 for *n*-butane and 0.044 for 1-butene. Our rate data for the paraffinic and olefinic hydrocarbons show that the total quenching of the $^3SO_2$ must have occurred in the equimolar 1-C_4H_8–SO_2 mixture, but in the *n*-butane–SO_2 mixture only 72% of the total $^3SO_2$ species formed would be quenched by *n*-C_4H_{10}. Therefore, the ratio of quantum yields of sulfinic acid formation for total quenching by the hydrocarbons (1-C_4H_8–*n*-C_4H_{10}) will be 0.138. Hence the corrected rates of $BuSO_2H$ formation can be calculated from the measured total rates (R_{tot}) as follows: $R_{BuSO_2H} = (R_{tot} - 0.138R^0{}_{BuSO_2H})/0.862$. The Dainton and Ivin data were taken from their Figure 12 for runs at the four lowest 1-C_4H_8 pressures.[6b] For these conditions the correction of the rate data is least serious. The magnitude of the *n*-butanesulfinic acid quantum yields of Dainton and Ivin is unexpected in terms of the theory which we have presented. However, the difficulty is not real since the absolute values appear to be in error. R. B. Timmons, *Photochem.*

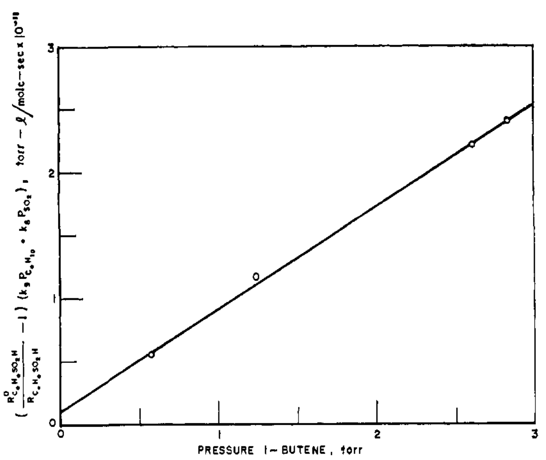

Figure 3. Plot of the function B of the text; data are from the full Hg-arc photolyses of SO_2–n-C_4H_{10} mixtures ($P_{SO_2} = P_{C_4H_{10}} = 150$ Torr) at 25° with added 1-butene, from Dainton and Ivin;[6b] the slope is related in theory to $k_{9a} + k_{9b}$ for 1-butene.

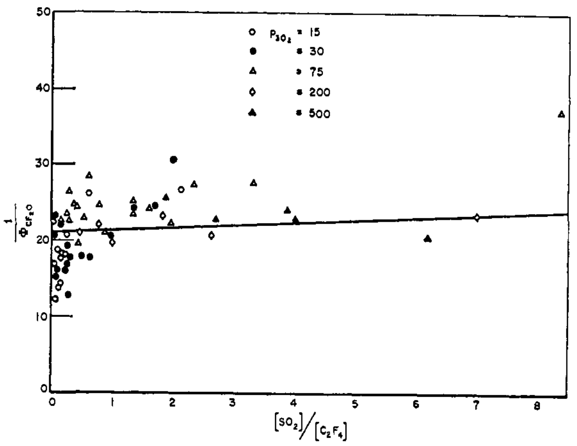

Figure 4. Plot of the function D of the text; data are from the 3130-Å photolyses of SO_2–C_2F_4 mixtures at 25° by Cehelnik, Spicer, and Heicklen.[8]

data and our measured $^3SO_2$ quenching rate constant data for n-C_4H_{10} [$(k_{9a} + k_{9b})_{C_4H_{10}} = 1.23 \times 10^9$] and SO_2 [$k_{8a} + k_{8b} = 3.9 \times 10^8$ l./(mol sec)] gave estimates of the left-hand side of relation B. This function has been plotted in Figure 3 *vs.* the added pressure of 1-butene. The theoretically expected linear form of the plot is evident. The slope is equal in theory to the total $^3SO_2$ quenching constant for 1-C_4H_8. The data give $(k_{9a} + k_{9b})_{C_4H_8} = (8.1 \pm 0.5) \times 10^{10}$ l./(mol sec). This is in excellent agreement with the value we have measured for the similar 1-olefin, propylene: $(k_{9a} + k_{9b})_{C_3H_6} = (8.5 \pm 0.9) \times 10^{10}$ l./(mol sec). It seems clear that the previously unexplained quantitative effect of 1-butene addition on the photochemical rates of sulfinic acid formation is readily understood in terms of the present $^3SO_2$ mechanism.

Dainton and Ivin's measured quantum yields of sulfinic acids formed from the olefins give us a measure of the efficiency of this chemical quenching mode. In terms of the present triplet mechanism the quantum yield of the sulfinic acids will be given by

$$\Phi_{RSO_2H} = \left(\frac{k_{9a}}{k_{9a} + k_{9b}}\right)\left(\frac{k_2}{k_1 + k_2}\right) \times \left(\frac{[RH](k_{9a} + k_{9b})}{[RH](k_{9a} + k_{9b}) + [SO_2](k_{8a} + k_{8b})}\right) \qquad \text{(C)}$$

For the experimental conditions chosen for measurements by Dainton and Ivin, equal pressures of SO_2 and olefin, $[RH](k_{9a} + k_{9b}) \gg [SO_2](k_{8a} + k_{8b})$, relation C reduces to: $\Phi_{RSO_2H} = [k_{9a}/(k_{9a} + k_{9b})][k_2/(k_1 + k_2)]$. Using the experimental estimate of $k_2/(k_1 + k_2) = 0.09 \pm 0.01$[10,24] and Φ_{RSO_2H} data of Dainton and Ivin, we estimate $k_{9a}/(k_{9a} + k_{9b}) = 0.14$, 0.22, 0.49, and 0.37 for ethylene, propylene, 1-butene, and 2-butene, respectively. Thus, the fraction of the total $^3SO_2$ quenching which leads to sulfinic acid products is appreciable. In the case of 1-butene, sulfinic acid formation accounts for about one-half of the total quenching.

The Cehelnik, Spicer, and Heicklen data from C_2F_4–SO_2 photolyses at 3130 Å can be used to test further the applicability of the triplet mechanism to the excited singlet SO_2–olefin systems.[8] One of the measured products in their experiments was CF_2O. Presumably this arises from the overall reaction 9a′ involving some excited state of sulfur dioxide (SO_2*). If the state re-

$$SO_2^* + C_2F_4 \longrightarrow CF_2O + SO + CF_2 \qquad \text{(9a}'\text{)}$$

sponsible here is the triplet sulfur dioxide, then our mechanism should apply, and relation D would be expected to describe the dependence of ϕ_{CF_2O} on the ratio of reactants.

$$\frac{1}{\Phi_{CF_2O}} = \left(\frac{k_1 + k_2}{k_2}\right) \times \left(\frac{k_{9a'} + k_{9a} + k_{9b}}{k_{9a}} + \frac{(k_{8a} + k_{8b})[SO_2]}{k_{9a}[C_2F_4]}\right) \qquad \text{(D)}$$

Here k_{9a} represents the rate constant for all chemical $^3SO_2$ quenching reactions other than $k_{9a'}$, and k_{9b} is the constant for the physical quenching reactions. The data of Cehelnik, *et al.*, are plotted in Figure 4 according to the functional form of relation D. The data are very scattered and reflect experimental complications present in this system. If one forces the least-squares linear fit to the data, the resulting line is $(1/\Phi_{CF_2O}) = (20.9 \pm 1.2) + (0.35 \pm 0.15)[SO_2]/[C_2F_4]$. From the slope and our measured values of $k_2/(k_1 + k_2)$ and $k_{8a} + k_{8b}$, we estimate $k_{9a'} = (1.3 \pm 0.6) \times 10^{10}$ l./(mol sec). Note that this value compares well with our measured value of $^3SO_2$ quenching by CF_2CHF, $k_9 = k_{9a} + k_{9b} = (1.1 \pm 0.1) \times 10^{10}$ l./(mol sec). From the intercept of the plot of Figure 4 we calculate $k_{9a'}/(k_{9a'} + k_{9a} + k_{9b}) = 0.53 \pm 0.07$. Both the value of $k_{9a'}$ and the estimated ratio of chemical to total quenching for $^3SO_2$ with C_2F_4 suggest that the triplet reaction scheme given here is applicable to the singlet excited SO_2–C_2F_4 system and that chemical quenching is an important part of the $^3SO_2$ quenching reactions with C_2F_4.

An additional test of the mechanism can be made using the data of Cehelnik, *et al.*, for the nitric oxide inhibition of the CF_2O formation in the 3130-Å photolysis of SO_2–C_2F_4 mixtures. If the triplet mechanism ap-

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Photobiol., 12, 219 (1970), reported recently $\Phi = 0.080$ for runs at 3130 Å and equal pressures of SO_2 and n-butane. Since only ratios of quantum yields appear in relation B, an absolute error in the Dainton and Ivin quantum yield data introduces no error in our rate constant estimate of k_9 for 1-butene.

plies, then the CF_2O quantum yield data for experiments with added NO should be given by

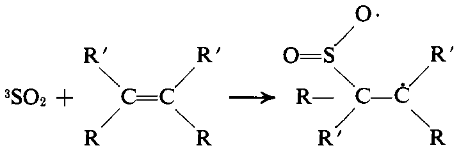
$$\left(\frac{\Phi^0_{CF_2O}}{\Phi_{CF_2O}} - 1\right)[P_{SO_2}(k_{8a} + k_{8b}) + P_{C_2F_4}k_{9(C_2F_4)}] = k_{9(NO)}P_{NO} \quad (E)$$

$\Phi^0_{CF_2O}$ is the quantum yield for experiments without added nitric oxide. This value was estimated for each $[SO_2]/[C_2F_4]$ ratio employed using the least-squares equation which describes the uninhibited photolysis data. Using our estimates of $k_{8a} + k_{8b} = 3.9 \times 10^8$ and the value for $k_9 = 1.3 \times 10^{10}$ l./(mol sec) which we estimated from the data of Cehelnik, *et al.*, we have tested the NO inhibition data according to the functional form of relation E. These data are plotted in Figure 5. The slope of the least-squares line for the data gives $k_{9(NO)} = (5.8 \pm 1.4) \times 10^{10}$ l./(mol sec). In view of the rather large scatter in the results of Cehelnik, *et al.*, this value is a reasonable check on that found directly in $^3SO_2$ lifetime studies: $k_{9(NO)} = (7.4 \pm 0.3) \times 10^{10}$ l./(mol sec).[26]

All of the previously published data for olefin–SO_2 photolyses within the first absorption band fit well the $^3SO_2$ mechanism suggested here. It seems likely that the only role of the excited singlet state in these systems is to provide the source of reactant $^3SO_2$ molecules through the intersystem crossing reaction 2.

The Detailed Mechanism of the $^3SO_2$–Olefinic Hydrocarbon Quenching Reactions. The results which we have discussed suggest that a large part, if not all, of the observed SO_2 triplet quenching is the result of a chemical interaction of the $^3SO_2$ and the olefin molecules. This was found to be the case as well for the 2400–3200-Å photolyses of SO_2–paraffin hydrocarbon systems where an H-atom abstraction mechanism seemed to fit best the experimental facts.[12] However, it is very unlikely that H-atom abstraction from the olefins is the rate-determining step in sulfinic acid formation in these systems. The rate of $^3SO_2$ reaction with the olefins is near the collision number and about 100 times faster than that observed for the paraffin hydrocarbons. Note that the rate constant for the olefin with the strongest C–H bonds, ethylene (4.4×10^{10}), is very much larger than that found with the paraffin with the weakest C–H bond, isobutane [0.16×10^{10} l./(mol sec)]. Obviously an H-atom abstraction by $^3SO_2$ cannot be important in the $^3SO_2$–olefinic hydrocarbon systems.

All of the present and previously published data for the excited SO_2–olefin systems seems to be in accord with the hypothesis of the quenching reaction proceeding through a highly polarized, charge-transfer-like intermediate formed between the $^3SO_2$ and the π system of the olefin. We suggest that this complex leads subsequently to an SO_2 addition to the olefinic double bond as observed in the O(^{3}P)-olefin reactions.[15]



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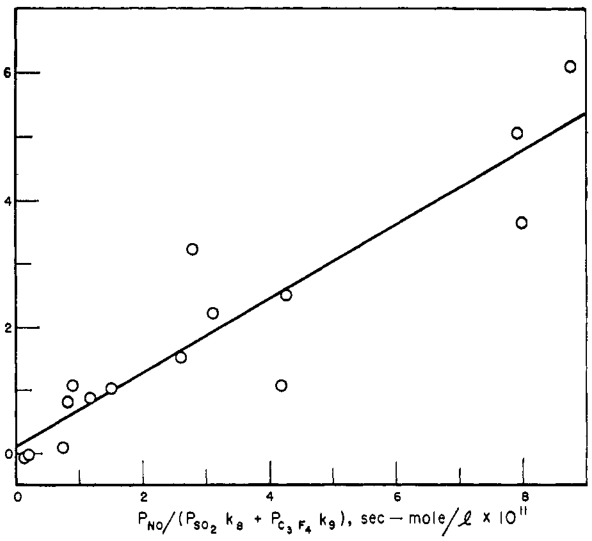

Figure 5. Plot of the function E of the text; data are from the nitric oxide inhibited, 3130-Å photolyses of SO_2–C_2F_4 mixtures at 25° from Cehelnik, Spicer, and Heicklen;[8] in theory the slope of the plot is equal to $k_{9a} + k_{9b}$ for nitric oxide.

One can rationalize all of the published results on excited SO_2–olefin systems in terms of alternate paths of decay of the intermediate triplet diradical **1** (Scheme I).

Among the alternative reaction paths of the intermediate diradical **1** is dissociation in path i; the net result of the $^3SO_2$ quenching by addition and subsequent dissociation in this case will be cis–trans isomerization, observed for the *cis*-2-butene compound by Bristow and Dainton[7a] and Cundall and Palmer.[7b] When the intermediate **1** contains α-H atoms, it may undergo an intramolecular H-atom abstraction reaction involving a six-membered ring intermediate in process ii. After spin inversion the reaction would lead to a β,γ-unsaturated sulfinic acid product. The very slow conversion of the 2-butene to 1-butene observed in the 2-butene–SO_2 experiments of Cundall and Palmer may occur from the subsequent H-atom transfer reaction iia. One would expect this reaction to be very slow compared to the cis–trans isomerization since the less favored four-center transition state is necessary. It may involve a heterogeneous route, either photochemical or thermal in origin.[7b] Reaction path iii represents the special case of an olefin which has no α-H atoms, as with ethylene. An alternative four-membered ring transition state may lead to the α,β-unsaturated sulfinic acid in this case. The quantum yield of sulfinic acid product from ethylene (0.013) is significantly lower than that for propylene (0.020); conceivably part of this difference results from the slowness of process iii relative to dissociation in i. An additional reaction of **1** is possible. The diradical may cyclize with spin inversion to form the four-membered-ring structure of an unidentified possible compound **2** in reaction path iv. Presumably the dissociation of **2** into more stable products would occur when the energetics of the process are favorable. The thermal dissociation into the original reactants may result, or when the R groups in the intermediate **1** are fluorine atoms as in C_2F_4, then CF_2O, CF_2, and SO may be formed efficiently as observed by Cehelnik, *et al.* Obviously in this case internal H-atom abstraction paths are impossible.

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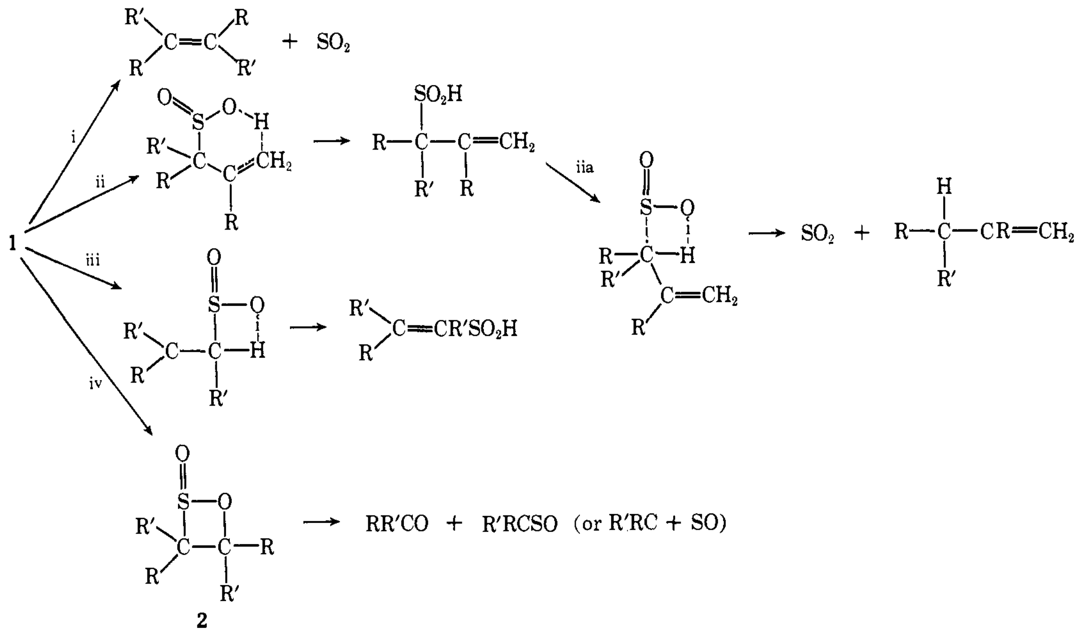
(26) H. W. Sidebottom, C. C. Badcock, G. E. Jackson, J. G. Calvert, G. W. Reinhardt, and E. K. Damon, *Environ. Sci. Technol.*, in press.

Scheme I



There are no product studies which can aid reasonable speculation on the mechanism operative in the $^3SO_2$ quenching reactions with aromatic molecules. However, it is conceivable that some type of metastable bicyclic addition compound is formed in these cases in a fashion analogous to that of the structures proposed for the charge-transfer complexes observed between ground-state SO_2 and the aromatic compounds.[27]

All of the information available on the excited SO_2–olefinic hydrocarbon reactions favors a mechanism choice similar to that suggested for the O(^3P) atom–olefin reactions studied by Cvetanović.[17] Since the reactions occur at rates near the collision number, it is likely that the activation energy is near zero, and the preexponential factor is near the collision number. If the rate-determining step is the nonspecific attack of the electrophilic $^3SO_2$ molecule on the olefinic double bond, these facts can be rationalized well.

We have initiated studies aimed at identification of the products of the $^3SO_2$–olefin reaction and the quantum yields with which they are formed. These data will be necessary to delineate further the nature of the reactions in this most interesting system. We are investigating the possibility of duplicating the $^3SO_2$–olefinic hydrocarbon reactions by direct excitation within the charge-transfer band of ground-state SO_2–unsaturated hydrocarbon mixtures.

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[27] L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, 73, 4169 (1951).