Mechanism of the Photolysis of Sulfur Dioxide–Paraffin Hydrocarbon Mixtures

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Abstract: The mechanism of the photochemical reactions of SO_2–hydrocarbon mixtures was studied through observations of the sulfur dioxide triplet ($^3SO_2$) molecule emission. The lifetimes of the phosphorescence decay of $^3SO_2$ were determined in SO_2–hydrocarbon mixtures. The triplet was excited directly using a 3828.8-Å laser pulse. The following bimolecular $^3SO_2$ quenching rate constants for the paraffin hydrocarbons were estimated from the slopes of plots of $1/\tau$ *vs.* the hydrocarbon pressure in experiments at constant pressure of SO_2 and a temperature of 25°: methane, $(1.16 \pm 0.16) \times 10^8$; ethane, $(2.09 \pm 0.21) \times 10^8$; propane, $(5.11 \pm 0.58) \times 10^8$; *n*-butane, $(12.3 \pm 1.7) \times 10^8$; isobutane, $(15.8 \pm 1.9) \times 10^8$ l./(mol sec). These data and a reaction mechanism suggested here fit well the previously published experimental product rate data of Dainton and Ivin and Timmons derived in SO_2–hydrocarbon mixture photolyses at 2400–3200 Å. It is concluded that the triplet molecule of sulfur dioxide is alone responsible for the photochemistry observed in SO_2–hydrocarbon mixture photolyses in both the first allowed and the "forbidden" absorption bands of SO_2. Speculation is given on the detailed mechanism of the $^3SO_2$ quenching reaction with the paraffin hydrocarbons.

The chemical reaction between photochemically excited sulfur dioxide and paraffin hydrocarbons has been studied by a number of investigators.[1-3] The SO_2–hydrocarbon system is extremely complex and very difficult to study experimentally. The nonvolatile products which settle out on the reaction vessel walls during the photolyses are difficult to identify conclusively, and the mechanism of the reaction remains uncertain. Dainton and Ivin[1a] presented considerable evidence that alkylsulfinic acids are the major products of the reaction. They found that the quantum yields were relatively small; in equimolar SO_2–RH mixtures the values varied from 0.006 for methane to 0.26 for pentane. Through pressure measurements, Dainton and Ivin found that the product quantum yield in *n*-butane–SO_2 mixture photolyses with a full Hg arc was insensitive to variations in $[SO_2]$ and temperature, but dependent on $[n\text{-}C_4H_{10}]$.[1b]

Recently Timmons has reported on a similar product rate study of SO_2–hydrocarbon systems excited at 3130 Å.[3] Although the results are qualitatively similar to those of Dainton and Ivin, there were some significant differences between the findings of the two groups. (1) Timmons found lower quantum yields of the photochemical products; from equimolar mixtures of SO_2 and RH, the highest quantum yield was 0.080 with *n*-butane. (2) The analytical data showed that the sulfinic acids are not the only compounds among the viscous, nonvolatile reaction products which formed. (3) In isobutane mixtures with SO_2, the ratios of reactants consumed, $-R_{SO_2}/-R_{RH}$, varied from unity for runs with $[SO_2] \leq [i\text{-}C_4H_{10}]$ to 2.8 with $[SO_2]/[i\text{-}C_4H_{10}] = 3.9$. (4) In contrast to the conclusions of Dainton and Ivin, Timmons found that the quantum yields were dependent on the $[SO_2]/[RH]$ reactant ratio, and they approached limiting values for $[RH] \gg [SO_2]$.

The nature of the excited state(s) of SO_2 responsible for the chemical reactions has been the subject of some discussion. Timmons found little suppression of the rate of product formation from isobutane–SO_2 mixtures upon adding methane gas at a pressure twice that of the isobutane used. Since methane quenches the excited singlet sulfur dioxide ($^1SO_2$) molecules much more effectively than it quenches the triplet sulfur dioxide ($^3SO_2$) molecules,[4] and yet it reacts only very inefficiently to form chemical products in the photolysis of SO_2–CH_4 mixtures, he concluded that the triplet sulfur dioxide molecule was the important reactant leading to product formation in the isobutane–SO_2 system. Johnston and Dev Jain[2] had hypothesized previously that the $^3SO_2$ species may be involved in this reaction. Their suggestion was based apparently on the observation of earlier workers that the quantum yield of products was small and more or less constant for the reactions of excited SO_2 with SO_2, O_2, and hydrocarbons. However, the quantum yield is neither small nor near constant for these various reactants, so the argument is inconclusive; the same results would be obtained if only the excited singlet molecules were involved in competitive reactions in which a fraction underwent chemical quenching but with the largest share quenched to the ground state.

Recently Okuda, Rao, Slater, and Calvert have shown conclusively that the $^3SO_2$ molecule is the photochemically active entity in sulfur dioxide photolysis.[5] They pointed out that it would be most interesting to determine the spin state of SO_2 responsible for sulfinic acid formation in SO_2–hydrocarbon mixture photolyses. They observed that the quantum yield of $^3SO_2$ formation from intersystem crossing was only 0.09 ± 0.01[6,7] for

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

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

[3] R. B. Timmons, *Photochem. Photobiol.*, **12**, 219 (1970).

[4] H. D. Mettee, *J. Phys. Chem.*, **73**, 1071 (1969).

[5] S. Okuda, T. N. Rao, D. H. Slater, and J. G. Calvert, *ibid.*, **73**, 4412 (1969).

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

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

excitation within the first allowed absorption band, yet the sulfinic acid product quantum yield was 0.26 in irradiated pentane–SO_2 equimolar mixtures.[1a] Unless a chain reaction is involved in some of these systems, the data suggest that the $^1SO_2$ state must be an important reactant, at least in some cases.

We initiated the present work to clarify the possible roles of the triplet and singlet excited SO_2 species in the SO_2–alkane reactions. We employed the 3828.8-Å laser system to excite directly the $^3SO_2$ within the "forbidden" $SO_2(^1A_1) \rightarrow SO_2(^3B_1)$ absorption band. The rate constants for the $^3SO_2$ quenching reactions of various hydrocarbons were determined from $^3SO_2$–lifetime measurements in SO_2–hydrocarbon mixtures. The present rate constant data can be used to account quantitatively for the chemical results of the previous investigations. The results also provide significantly new insight into the mechanism of photoexcited sulfur dioxide with the paraffin hydrocarbons.

Experimental Section

The sulfur dioxide triplet state was 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 equipment and the methods employed have been described in detail previously[8,9] and need not be considered further here. The reactant hydrocarbons employed were the high-purity products of the Phillips Petroleum Co. or the Matheson Chemical Co. The sulfur dioxide was the anhydrous product of Matheson. All reagents were purified further and degassed by bulb-to-bulb distillation in the vacuum line in which they were stored after purification.

Table I. The Inverse Lifetimes of Sulfur Dioxide Triplet Molecules in Mixtures of Sulfur Dioxide (1.55 Torr) with Some Paraffin Hydrocarbons at 25°

P_{RH}, Torr	$1/\tau$, sec^{-1} × 10^{-4}	P_{RH}, Torr	$1/\tau$, sec^{-1} × 10^{-4}
(a) Methane		(d) *n*-Butane	
0.00	4.13	0.000	4.09
1.55	4.93	0.191	5.44
2.59	5.63	0.298	7.19
4.09	7.22	0.392	7.88
4.94	7.18	0.505	7.51
5.88	7.10	0.618	8.23
7.18	8.91	0.740	10.73
7.97	8.84	0.917	10.74
9.41	10.10	0.945	10.85
		1.03	10.32
(b) Ethane		1.38	13.70
0.00	4.18	1.40	14.07
0.441	4.55		
1.98	5.45	(e) Isobutane	
3.03	7.16	0.000	4.39
4.53	9.19	0.134	4.85
5.43	9.54	0.212	5.74
6.40	11.11	0.334	6.26
7.23	12.28	0.424	8.01
		0.527	8.22
(c) Propane		0.636	10.12
0.00	4.21	0.727	9.33
0.307	4.67	0.848	11.97
0.614	5.67	0.919	10.67
1.02	7.33	1.06	13.30
1.52	8.19	1.11	13.70
1.85	8.58		
2.20	10.94		
2.42	10.97		
3.01	11.46		
3.48	14.06		

The gaseous mixtures were prepared in a mercury-free system using a Pyrex spiral manometer as a null instrument to measure reactant pressures. Mixing of the two reactants was effected with a thermal gradient pump which was in series with the photolysis cell.

Some idea of the reproducibility of the measurements of reactant pressure and $^3SO_2$ lifetimes is had in a comparison of the lifetimes estimated for pure SO_2 at 1.55 Torr in runs at the start of the five reactant series studied (Table I). The values are near equal as one would hope if the experimental methods were working satisfactorily. The average value, $1/\tau = (4.20 \pm 0.24) \times 10^4$ sec^{-1}, checks well within the experimental error with the estimate, $1/\tau = (3.97 \pm 0.54) \times 10^4$ sec^{-1}, derived for $P_{SO_2} = 1.55$ Torr from the least-squares equation for $1/\tau$ *vs.* P_{SO_2} (0.16–17.6 Torr) derived by Sidebottom, *et al.*[9] A further check on the consistency of the lifetime data is seen in the near constancy of the least-squares intercepts of the Stern–Volmer plots of $1/\tau$ *vs.* P_{RH}; see the data of Table II. The lines were not forced through the measured value for $1/\tau$ at $P_{RH} = 0$. The average value of these intercepts, $1/\tau = (4.11 \pm 0.55) \times 10^4$ sec^{-1}, is again equal within the experimental error to the other estimates of this quantity.

Discussion

The Determination of the $^3SO_2$ Quenching Rate Constants for the Paraffin Hydrocarbons. The formation, decay, and the quenching reactions of the excited singlet ($^1SO_2$) and triplet ($^3SO_2$) sulfur dioxide species are described well by an extension of the previously proposed reaction sequence,[6,8] where RH represents the added hydrocarbon quenching gas.

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

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

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

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

$${}^1SO_2 + RH \longrightarrow (RSO_2H \text{ or } SO_2 + RH) \qquad \text{(1b)}$$

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

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

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

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

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

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

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

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

$${}^3SO_2 + RH \longrightarrow RSO_2H \qquad \text{(9a)}^{10}$$

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

In the previous studies of SO_2–RH systems the excitation was effected by irradiation within the first allowed absorption band (2400–3200 Å), and the entire rather complex sequence of reactions I, 1a–9b must be considered in the treatment of the experimental results. In the next section we will deal with such systems in the explanation of the SO_2–RH mixture photolyses at 2400–3200 Å. In this work excitation at 3828.8 Å created $^3SO_2$ species, unaccompanied by $^1SO_2$ and its complicating series of reactions. For our case the primary reaction was followed by only reactions 6–9b. From this reaction mechanism one expects the $^3SO_2$ lifetime

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

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

(10) The sulfinic acid formation may not proceed directly as an SO_2 insertion reaction; see text. However, we shall assume the rate-determining step in its formation is a bimolecular reaction involving photoexcited SO_2 and hydrocarbon molecules.

in mixtures of SO_2 and RH to be given by the simple relation A.

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

We have determined lifetimes of $^3SO_2$ phosphorescence emission in runs at fixed SO_2 pressure (1.55 Torr) and with varied pressure of the added hydrocarbon quencher gas; these data are summarized in Table I. For our conditions an estimate of $k_9 = k_{9a} + k_{9b}$ can be made from the slopes of the $1/\tau$ *vs.* P_{RH} plots in Figure 1. The parameters which determine the least-squares lines in the Stern–Volmer plots are summarized in Table II together with the estimates of the quenching rate constants, $k_9 = k_{9a} + k_{9b}$.

Table II. Summary of the Quenching Rate Constant Data for Sulfur Dioxide Triplet Molecules with Various Paraffin Hydrocarbons at 25°

Compound	Parameters of the Stern–Volmer plots[a] Intercept, $sec^{-1} \times 10^{-4}$	Slope, $(mm\ sec)^{-1} \times 10^{-4}$	k_9, l./(mol sec) $\times 10^{-8}$
Methane	4.09 ± 0.48	0.624 ± 0.085	1.16 ± 0.16
Ethane	3.85 ± 0.58	1.12 ± 0.11	2.09 ± 0.21
Propane	4.09 ± 0.62	2.75 ± 0.31	5.11 ± 0.58
n-Butane	4.57 ± 0.64	6.64 ± 0.90	12.3 ± 1.7
Isobutane	3.96 ± 0.71	8.5 ± 1.0	15.8 ± 1.9

[a] Derived from the least-squares treatment of the $1/\tau$ *vs.* pressure of hydrocarbon plots of Figure 1 and the data of Table I; the error limits reported are the 95% confidence limits (twice the standard deviation).

A comparison of the data for the different paraffin hydrocarbons shows some interesting variations of the quenching rate constants with hydrocarbon structure. In general the paraffins have quenching constants which are several orders of magnitude smaller than those with $^1SO_2$ species.[4,6,11] However, they increase regularly as the complexity of the hydrocarbon increases: $k_9 = 1.2 \times 10^8$ for CH_4 to 15.8×10^8 l./mol sec) for *i*-C_4H_{10}.

It is interesting and significant to the mechanistic considerations that the order of increasing $^3SO_2$ quenching facility with altered hydrocarbon structure is the same as that observed for H-atom abstraction reactions of atoms and free radicals with these hydrocarbons. Note in Table III the comparison of the rate constants for $^3SO_2$ and Hg($^3P_1$) quenching reactions with those of H abstraction by F, Cl, Br, H, and CH_3. It can be seen that the sulfur dioxide triplet is a very reactive species compared to the free radicals. Among those compared in Table III, only the F and Cl atoms have rates of reaction greater than those of $^3SO_2$ quenching with a given hydrocarbon. The $^3SO_2$ species appears to be most like the Hg($^3P_1$) atom in its reaction rates with RH, although it is less selective than Hg($^3P_1$) in the cases of CH_4, C_2H_6, and C_3H_8, and it is quenched by a given hydrocarbon about 10–30 times less efficiently than Hg($^3P_1$). In the case of the Hg($^3P_1$) atom, chemical quenching through H-atom abstraction from the hydrocarbon (RH), with ultimate H and R radical formation, accounts well for the total quenching rates measured.[12] By analogy one might suggest that $^3SO_2$ quenching by RH results from H-atom abstraction. However, such a conclusion is premature since the alternative mechanism of SO_2 insertion might be expected to show the trend in rates observed as well. We will consider the alternative mechanisms after a more detailed examination of the photolysis data of Dainton and Ivin[1] and Timmons.[3] Their data, together with our present results, give additional insight into the mechanism of the excited-SO_2 reactions with hydrocarbons.

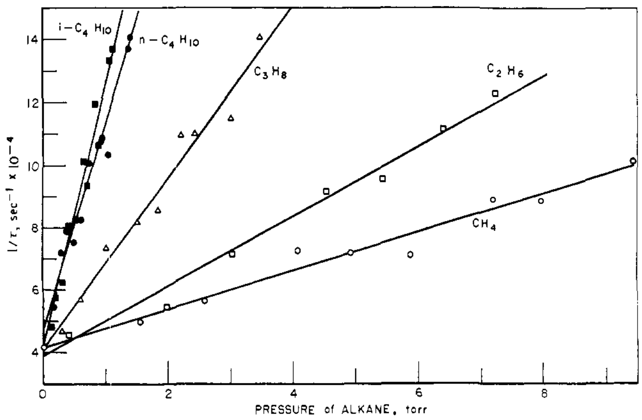

Figure 1. Stern–Volmer plots for the $^3SO_2$ quenching reactions of some of the paraffin hydrocarbons; data are from the 3828.8-Å laser-excited-SO_2 experiments at 25°: ○, CH_4; □, C_2H_6; Δ, C_3H_8; ●, *n*-C_4H_{10}; ■, *i*-C_4H_{10}.

The Nature of the Primary Products of the Excited-SO_2 Reactions with Paraffin Hydrocarbons. A real concern in the interpretation of the rate studies of the excited-SO_2–RH system is the uncertainty which exists in the nature of the products. This is especially true since both Dianton and Ivin[1] and Timmons[3] measured pressure changes to follow the rates of product formation. Let us review briefly the pertinent evidence concerning the chemical nature of the products. Dainton and Ivin concluded from the observed reactant stoichiometry (one sulfur dioxide to one RH used), the analytical data for the chemical composition of the products, and the acidic properties of the products, that sulfinic acids (RSO_2H) are the major products formed.[1a] Timmons has questioned this conclusion since the only pure sulfinic acids prepared to date (*n*-butanesulfinic acid, *n*-octanesulfinic acid,[13] and methanesulfinic acid[14]) are thermally unstable solids.[3] In addition both Johnston and Dev Jain[2] and Timmons[3] found that a great number of unidentified different products result from these SO_2–RH reactions. However, in the previous studies product analysis was carried out on the products resulting from very long runs in which extensive conversion of the reactants was allowed. There is no assurance that the products found were primary products. Both Dainton and Ivin and Timmons observed the stoichiometric ratio of one SO_2 removed per molecule of RH reacted when $[SO_2] < [RH]$. However, Timmons found that for runs with $[SO_2] \geq [RH]$ the ratio of reactants used $(-R_{SO_2}/-R_{RH})$ always exceeded unity. It should be noted that this observation does in no way exclude the contention of Dainton and Ivin that the sulfinic acids are the major products of excited SO_2 and hydrocarbon. Thus one expects the ratio

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[11] S. J. Strickler and D. B. Howell, *J. Chem. Phys.*, 49, 1947 (1968).

[12] R. J. Cvetanovic, *Progr. React. Kinet.*, 2, 39 (1964).

[13] H. Reinheckel and D. Jahnke, *Chem. Ber.*, 99, 1718 (1966).

[14] F. Wudl, D. A. Lightner, and D. J. Cram, *J. Amer. Chem. Soc.*, 89, 4099 (1967).

Table III. Comparison of the Rate Constants for the $^3SO_2$ and Hg($^3P_1$) Quenching Reactions of the Paraffin Hydrocarbons with Those for the H-Atom Abstraction Reactions, RH + X → R + XH (9), for H, F, Cl, Br, and CH_3 Radicals at 25°[a]

	X						
RH	$^3SO_2$ $k_9 \times 10^{-8}$	Hg($^3P_1$)[b] $k_9 \times 10^{-9}$	F[c,d] $k_9 \times 10^{-10}$	Cl[c] $k_9 \times 10^{-10}$	Br[c] $k_9 \times 10^{-3}$	H[e] $k_9 \times 10^{-5}$	CH_3 $k_9 \times 10^0$
CH_4	1.16	1.1	1.6	0.0037	0.000004	0.000083	0.010[f]
C_2H_6	2.09	1.5	3.7	1.6	0.015	0.085	2.5[g]
C_3H_8	5.11	18.0	4.6	4.4	2.5	1.0	22[h]
n-C_4H_{10}	12.3	40.0	5.2	8.2	7.3	1.0	76[i]
i-C_4H_{10}	15.8	50.0	5.2	4.8	62	5.3	288[h]

[a] Rate constants for reaction 9, l./(mol sec) × factor shown. [b] Data from the summary table, ref 12. [c] G. C. Fettis and J. H. Knox, *Progr. React. Kinet.*, **2**, 1 (1964). [d] A. F. Trotman-Dickenson and G. S. Milne, "Tables of Bimolecular Gas Reactions," NSRDS-NBS No. 9, 1967. [e] B. A. Thrush, *Progr. React. Kinet.*, **3**, 63 (1965). [f] J. R. McNesby and A. S. Gordon, *J. Amer. Chem. Soc.*, **76**, 4196 (1954). [g] J. R. McNesby, *J. Phys. Chem.*, **64**, 1671 (1960). [h] W. M. Jackson, J. R. McNesby, and B. deB. Darwent, *J. Chem. Phys.*, **37**, 1610 (1962). [i] J. R. McNesby and A. S. Gordon, *J. Amer. Chem. Soc.*, **78**, 3570 (1956).

of reactants used ($-R_{SO_2}/-R_{RH}$) to be greater than unity as $[SO_2] \geq [RH]$, since the $^3SO_2$–SO_2 reaction 8a would compete under these circumstances; $k_{8a} \cong k_{8a} + k_{8b}$,[5] and SO_2 will be removed as SO_3 and SO in these SO_2-rich mixtures. In fact, Timmons' observation that the rate of SO_2 removal was six times the rate of SO_3 formation in an equimolar mixture of SO_2 and isobutane is in excellent accord with the theoretically expected ratio of these rates. A ratio of 5.1 would be anticipated theoretically from our rate data provided that the $^3SO_2$ quenching by both SO_2 and RH is largely chemical in nature; this appears to be the case (see the following section).

The argument that the sulfinic acids are thermally unstable is also of little weight in excluding sulfinic acid formation in these photochemical studies; the formation of thermally unstable primary products is not uncommon to photochemical systems. The variety of secondary products that would form in thermal and photochemical decompositions could help explain the number of minor products found by Timmons[3] and Johnston and Dev Jain.[2]

All of the evidence suggests that the major product of the excited SO_2–RH reaction is a strong organic acid having $pK_a \cong 2$. It is difficult to imagine what other product than sulfinic acids would have these properties and would be formed when one molecule of SO_2 couples with each molecule of hydrocarbon.[15] The role of the SO_3 and SO products in the reactions at high $[SO_2]/[RH]$ is uncertain. SO_3 might be expected to react with the sulfinic acids and contribute to the general mix of materials which make up the impure liquid product of the photochemical runs.

In view of all the evidence it seems likely to us that the sulfinic acids are the major primary products of these experiments. It is also apparent that the quantitative consideration of the chemical reaction rate data should be restricted to those experiments at $[SO_2]/[RH] \leq 1$, since complications arising from SO_3 and SO will be minimized for these conditions.

The Mechanism of the SO_2–RH Mixture Photolyses at 2400–3200 Å. From the present rate data and the mechanism suggested we can attempt to predict the theoretically expected quantum yields of sulfinic acid formation. Some simplification of the complex mechanism can be made in our first efforts to fit the rate data. (1) If we consider only experiments carried out at pressures above 5 Torr, then the rates of reactions 3, 4, and 5 of the $^1SO_2$ species and 6 and 7 for the $^3SO_2$ molecules will be negligible compared to the other reactions of these molecules. (2) As a first approximation, we may assume that sulfinic acid products result only from the reactions of the $^3SO_2$ species and that none is derived from the $^1SO_2$ in reaction 1a. (3) We may postulate further that the fraction of $^1SO_2$ quenching collisions with RH which result in spin inversion, $k_2/(k_1 + k_2)$, is equal to that fraction measured in singlet SO_2–SO_2 quenching collisions (0.09 ± 0.01). For these conditions we can predict that the quantum yield of RSO_2H formation should be given by relation B. It is instructive to attempt to fit the most reliable data of Dainton and Ivin and Timmons (that from runs with relatively low $[SO_2]/[RH]$ ratios) to the form of relation B. We have used Dainton and Ivin's quantum yield data from SO_2–n-butane photolyses at 50 and 25 Torr of SO_2 in which the $[SO_2]/[RH]$ ratios varied over the range 0.087–4.0;[1b] Timmons' data for isobutane–SO_2 mixture photolyses were used for experiments with $[SO_2]/[RH]$ in the range of 0.51–1.59. These data are plotted in Figure 2 according to the functional form of relation B. Note in this figure that each set of data fits the linear form demanded by the theoretical function. Observe as well that Timmons' data from runs at temperatures of 25, 65, 100, and 150° all fit the same line within the experimental error. The least-squares line through the data of Dainton and Ivin is given by $(1/\Phi_{RSO_2H}) = 4.2 \pm 1.8 + (3.3 \pm 1.0)[SO_2]/[n\text{-}C_4H_{10}]$; the equation for Timmons data is $(1/\Phi_{RSO_2H}) = 11.8 \pm 0.7 + (3.4 \pm 0.8)[SO_2]/[i\text{-}C_4H_{10}]$.

$$\frac{1}{\Phi_{RSO_2H}} = \left(\frac{k_1 + k_2}{k_2}\right)\left(\frac{k_{9a} + k_{9b}}{k_{9a}}\right)\left(1 + \frac{(k_{8a} + k_{8b})[SO_2]}{(k_{9a} + k_{9b})[RH]}\right) \quad \text{(B)}$$

In theory we can calculate an estimate of k_{9a} for n-C_4H_{10} and i-C_4H_{10} from the slopes of these plots: $k_{9a} = [(k_{8a} + k_{8b})/(\text{slope of Figure 2})][(k_1 + k_2)/k_2]$. If we employ the best estimates of $k_{8a} + k_{8b} = (3.9 \pm 0.1) \times 10^8$ l./(mol sec)[8,9] and $k_2/(k_1 + k_2) = 0.09 \pm 0.01$,[6,7] then we calculate from the slopes of the plots of Figure 2 the following estimates of k_{9a} for n-butane and isobutane: for n-C_4H_{10}, $k_{9a} = (1.3 \pm 0.4) \times 10^9$ l./(mol sec); for i-C_4H_{10}, $k_{9a} = (1.3 \pm 0.3) \times 10^9$ l./(mol sec). Note that these estimates are equal within experimental error to the values found for the total quenching con-

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(15) The possible product of a chain reaction sequence RSO_2SO_2R would fit the observed stoichiometry of the excited SO_2–RH reaction, but it would not possess the acidic character required by the experimental evidence.

stants for these hydrocarbons in this work: for *n*-butane, $k_{9a} + k_{9b} = (1.2 \pm 0.2) \times 10^9$; for isobutane, $k_{9a} + k_{9b} = (1.6 \pm 0.2) \times 10^9$ l./(mol sec).

In theory the intercepts of the plots of Figure 2 are equal to $[(k_{9a} + k_{9b})/k_{9a}][(k_1 + k_2)/k_2]$. Using the experimental values for $k_1/(k_1 + k_2)$ we estimate from the intercepts: for $n\text{-}C_4H_{10}$, $k_{9a}/(k_{9a} + k_{9b}) = 2.6 \pm 1.2$; for $i\text{-}C_4H_{10}$, $k_{9a}/(k_{9a} + k_{9b}) = 0.94 \pm 0.12$. The error limits shown result from a consideration of random scatter only; thus the theoretically impossible lower limit for the ratio with $n\text{-}C_4H_{10}[k_{9a}/(k_{9a} + k_{9b}) \simeq 1.4]$ is considered to be near unity within the true experimental error. In fact, all of the data suggest that $k_{9a} \simeq k_{9a} + k_{9b}$, at least for the cases of *n*-butane and isobutane. Chemical quenching is the major origin of quenching of $^3SO_2$ observed with the butanes.

The fact that the Timmons' data from experiments at several temperatures fit the same line, coupled with our conclusion that $k_{9a} \cong k_{9a} + k_{9b}$, suggests that the activation energy of the $^3SO_2$ quenching reactions with SO_2 and RH are nearly equal. This conclusion is in fact borne out by the recent work of Otsuka.[16] His preliminary results give the following activation energies for the $^3SO_2$ quenching reactions with SO_2, C_2H_6, and C_3H_8, respectively: 2.8 ± 0.7, 3.0 ± 0.5, and 2.8 ± 0.5 kcal/mol.

A further critical test of the application of the triplet mechanism to the SO_2–RH mixture photolyses at 2400–3200 Å is possible using our rate constant data. We may calculate the theoretical quantum yields of sulfur dioxide triplets which are quenched by the various hydrocarbons using relation B. These data are shown in Table IV for the case of equimolar mixtures of SO_2 and RH. A comparison can be made of these theoretical values with the experimentally measured sulfinic acid quantum yields reported by previous workers. In general there is excellent agreement between those values calculated from relation B and the measured values of Timmons. The Dainton and Ivin data for C_2H_6 check well with theory and with Timmons' estimate, but the values for the higher hydrocarbons are significantly larger. The origin of the difference between the two experimental estimates is not clear. If H abstraction by $^3SO_2$ best describes the primary reaction in these systems, then it is possible, but not probable, that the results differ because of the formation of sulfinic acid in reactions of different chain length for the different conditions employed by the two research groups. This explanation is unlikely since the full Hg arc intensities employed by Dainton and Ivin should be considerably higher than the 3130-Å intensities used by Timmons, and the chains, if present, should be shorter in the experiments of Dainton and Ivin. It seems more likely to us that the differences arise because of experimental difficulties in the estimation of the absorbed light intensity in these runs in which product deposition on the windows of the cell is a serious factor.

Table IV. Comparison of the Theoretical and Measured Quantum Yields of RSO_2H Product in the Photolysis of SO_2 in Equimolar Mixtures of Hydrocarbon (RH) and SO_2

RH	$\Phi_{^3SO_2-RH}$[a]	Φ_{RSO_2H}[b]	Φ_{RSO_2H}[c]
CH_4	0.020	<0.01	0.006
C_2H_6	0.031	0.026	0.025
C_3H_8	0.051	0.045	0.125
$n\text{-}C_4H_{10}$	0.068	0.080	0.18
$i\text{-}C_4H_{10}$	0.072	0.071	0.23

[a] The theoretical quantum yield of $^3SO_2$ molecules which are quenched by RH as calculated from relation B for equimolar SO_2–RH mixtures using the rate constants from this work. [b] Experimental values as estimated by Timmons from pressure measurements made in 3130-Å photolyses of SO_2 in equimolar mixtures with RH. [c] Experimental values as estimated by Dainton and Ivin from pressure measurements in the full-mercury-arc photolyses of SO_2 in equimolar mixtures with RH.

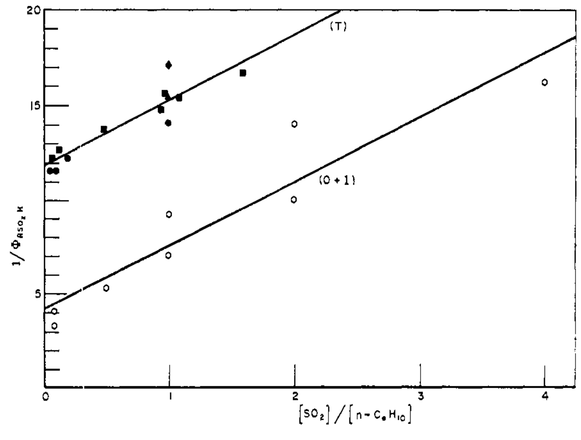

Figure 2. Plot of the inverse quantum yield of sulfinic acid *vs.* the $[SO_2]/[RH]$ ratio from photolyses of SO_2–hydrocarbon mixtures by Timmons[3] (T) and Dainton and Ivin[1] (D + I); Timmons' results are from the 3130-Å photolysis of isobutane–SO_2 mixtures at 25° (●), 65° (▲), 100° (■), and 150° (◆); Dainton and Ivin's results are from the full Hg-arc photolysis of *n*-butane–SO_2 mixtures at 25° (○).

Several important conclusions can be made in light of these results. (1) The involvement of the triplet sulfur dioxide molecule in the paraffin hydrocarbon–SO_2 mixture photolyses within the first allowed absorption band (2400–3200 Å) is clear. The results of the chemical studies are nearly quantitatively explicable without invoking the participation of the excited singlet molecules in RSO_2H formation. It appears that the only role of the $^1SO_2$ species in these systems is that of supplying the $^3SO_2$ molecules through the intersystem crossing reaction 2. (2) The fraction of the $^1SO_2$-quenching collisions which result in reaction 2 appears to be nearly constant for the hydrocarbons studied and nearly equal to that found for SO_2 quenching collisions. (3) There is little contribution by physical processes to the overall quenching rate of $^3SO_2$ by the hydrocarbons C_2H_6, C_3H_8, $n\text{-}C_4H_{10}$, and $i\text{-}C_4H_{10}$. Chemical quenching rate constants are near or equal to the measured triplet quenching rate constants for all of these hydrocarbons. (4) In the case of methane the $^3SO_2$ quenching may be largely physical in nature; the quenching rate constant is much larger than the chemical rate constant in this case. This conclusion is further supported by our rate data and another of Timmons' observations. For an isobutane-SO_2 equimolar mixture in which $\Phi_{RSO_2H} = 0.070$, he found that added methane with $[CH_4]/[i\text{-}C_4H_{10}] = 2$ lowered the yield to 0.058. If physical quenching dominates for CH_4–$^3SO_2$ interactions, then our quenching rate constant data suggest that the quantum yield for the experiment with added CH_4 would be $\Phi_{RSO_2H} = (15.8 + 3.9)\ (0.070)/$

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[16] K. Otsuka and J. G. Calvert, manuscript in preparation.

$[2(1.16) + 15.8 + 3.9] = 0.063$; this is in good agreement with the observed value.

The Detailed Mechanism of Sulfinic Acid Formation. There are two obvious alternatives to the mechanism of sulfinic acid formation in the overall reaction 9a. The reaction may involve a true $^3SO_2$ insertion into the C–H bond of the hydrocarbon, or the overall chemical reaction may be the result of an initial H-atom abstraction by $^3SO_2$.

$$\text{insertion} \quad {}^3SO_2 + RH \longrightarrow RSO_2H \qquad (9a')$$

$$\text{abstraction} \quad {}^3SO_2 + RH \longrightarrow SO_2H + R \qquad (9a'')^{17}$$

Timmons argued that the free-radical path is unlikely for several reasons. (1) Gaseous products such as hydrogen and the disproportionation and combination of free radicals R are not seen. (2) No appreciable temperature dependence of product formation is found, although Timmons expects one if a free-radical chain reaction is important. Neither of these arguments is compelling, particularly the first. Actually, Timmons reported the formation of small amounts of 2,2,3,3-tetramethylbutane and isobutene in the SO_2–isobutane experiments and small amounts of C_8 hydrocarbons in the *n*-butane–SO_2 experiments. He found also that reactions at higher temperatures tended to produce somewhat larger amounts of the C_8 hydrocarbons. These are precisely the results we would expect from the occurrence of reaction 9a''; the combination and disproportionation reactions of the R radicals would be relatively unimportant with reaction 10 dominating.

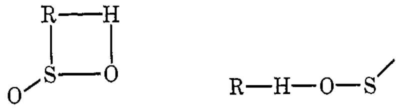
$$R + SO_2 \longrightarrow RSO_2 \qquad (10)$$

Sulfur dioxide is an excellent free-radical trap at the SO_2 concentrations and the temperatures used by previous workers.[18,19] The rate constants for CH_3 addition to SO_2 is equal to that for the very fast reaction, $CH_3 + O_2 \rightarrow CH_3O_2$, at 25°.[19] If reaction 9a'' were important then the major reaction of the radicals R would be with SO_2, reaction 10.

If the abstraction mechanism is the correct choice for these systems, then the disproportionation and combination of the RSO_2 and HSO_2 radicals must be favored over H abstraction from RH, since no chain reaction is evident. This is probably a reasonable requirement for the light intensities and temperatures employed. According to this scheme the sulfinic acid product would arise presumably from the RSO_2–SO_2H disproportionation reaction. In addition to the alkylsulfinic acids one might expect to find at least small amounts of products such as RSO_2SO_2R and RSO_2-SO_2H. The latter compound could not be important for the runs in which the one-to-one reactant stoichiometry was observed.

It should be made clear that the temperature independence of the quantum yields of RSO_2H gives no clue as to the temperature dependence of reactions 9a' or 9a''. In all of the previous studies there was competition between SO_2 and RH as quenchers for $^3SO_2$. Since the activation energies of these two reactions are nearly equal,[16] no temperature dependence would be expected for either mechanism choice. For this to be the case with the abstraction mechanism, we must demand that the length of the chain remain small for all the conditions used.

It is instructive to compare the transition states for the two possible rate-determining steps in the alternative mechanisms



insertion abstraction

From Otsuka's measured activation energies[16] and our rate data we can estimate the magnitude of the preexponential factors for reactions 9a: $\log A_{9a}$ [l./(mol sec)] = 9.28 for ethane and 9.60 for propane. Compare these estimates with those for the corresponding reactions of the CH_3 radical, the species of molecular complexity most similar to that of SO_2 for which we have H-abstraction data: $\log A_9$ [l./(mol sec)] = 9.3 for the reaction with C_2H_6[20] and 8.91 for the reaction with C_3H_8.[21] These values are reasonably close to those for the estimated reactions. On the other hand, the data do not fit well with the theoretically expected preexponential factor for the insertion reaction. In this case the rigid four-center transition state anticipated for the SO_2 insertion mechanism, coupled with the added requirement for spin inversion for this model, would result in an A factor considerably smaller than that found experimentally for the SO_2–RH systems. A value of $\log A_{9a'} \leq 7$ would be a reasonable estimate.

It is difficult to test the compatibility of Otsuka's measured small activation energy for reaction 9 involving C_2H_6 and C_3H_8 (3 kcal/mol) with that expected for the two alternative models, since the heat of formation of the sulfinic acids and the structure and thermochemistry of the SO_2H species have not been investigated to our knowledge. However, a reasonable estimate of the thermal data suggests that the insertion reaction 9a' for ethane would form the ethanesulfinic acid initially with about 110 kcal/mol excess energy.[22] This vibrational excitation could rupture the C–S bond in $C_2H_5SO_2H$ formed in experiments at low pressure if the insertion mechanism occurs.

Reasonable estimates of the thermal data for SO_2H suggest that reaction 9a'' would be exothermic by about 49 kcal/mol.[23] This is certainly consistent with the measured small value of the activation energy for the reaction.

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(17) The initiating reaction 9a'' is preferred to one of those suggested by Y. Ogata, Y. Izawa, and T. Tsuda, *Tetrahedron*, 21, 1349 (1965); they suggest $SO_2^* + RH \rightarrow SO_2 + R + H$. This reaction is highly endothermic for $^3SO_2$; $\Delta H \cong$ 18–31 kcal/mol for the hydrocarbons employed here.

(18) J. A. Good and J. C. J. Thynne, *Trans. Faraday Soc.*, 63, 2708, 2720 (1967).

(19) 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.

(20) Reference *g* in Table III.

(21) Reference *h* in Table III.

(22) This estimate was made using standard enthalpy data and the following estimated enthalpy changes (kcal/mol): $C_2H_5SO_2H \rightarrow C_2H_5SO_2 + H$, 111 [the value suggested for $CH_3CO_2H \rightarrow CH_3CO_2 + H$ by L. Jaffe, E. J. Prosen, and M. Szwarc, *J. Chem. Phys.*, 27, 416 (1957)]; $C_2H_5SO_2 \rightarrow C_2H_5 + SO_2$, 23 [the value suggested for $CH_3SO_2 \rightarrow CH_3 + SO_2$ by W. K. Busfield, K. J. Ivin, H. Mackle, and P. A. G. O'Hare, *Trans. Faraday Soc.*, 57, 1064 (1961)]; $SO_2 \rightarrow {}^3SO_2$, 73.7 (G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polatomic Molecules," Van Nostrand, Princeton, N. J., 1966, p 605).

(23) This estimate was made assuming the following change in enthalpy together with the data of ref 22 and standard enthalpy data: $C_2H_5SO_2H \rightarrow C_2H_5 + SO_2H$, 61 kcal/mol [the value for $CH_3SO_2CH_3 \rightarrow CH_3 + SO_2CH_3$ from W. K. Busfield and K. J. Ivin, *Trans. Faraday Soc.*, 57, 1044 (1961)].

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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