Acknowledgment.—The authors wish to thank Professor V. N. Ipatieff for the encouragement and the interest shown in the progress of this investigation.

Summary

Exchange reaction between hydrogen of butanes and deuterium of deuterium bromide–aluminum bromide catalyst has been studied in order to elucidate the mechanism of butane isomerization.

Very little exchange reaction and no isomerization occurred when butanes were treated with deuterium bromide–aluminum bromide. In the presence of 0.1 mole per cent. of butenes, isomerization of *n*-butane to isobutane occurred and 82–92% of the deuterium was exchanged for hydrogen.

Deuteroxyaluminum dibromide acted as a catalyst for the isomerization of *n*-butane; less than 6% of the deuterium underwent an exchange reaction.

Mechanism of isomerization of butanes was discussed.

CHICAGO, ILLINOIS RECEIVED AUGUST 5, 1946

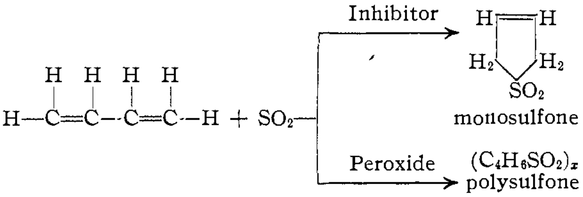
[CONTRIBUTION FROM THE PHYSICAL RESEARCH LABORATORY OF THE DOW CHEMICAL CO.]

Kinetics of the Diene Sulfur Dioxide Reaction[1]

BY L. R. DRAKE, S. C. STOWE AND A. M. PARTANSKY[2]

Introduction

It is well known in the literature[3] that conjugated dienes react in the liquid phase with sulfur dioxide to form sulfones. The course of the reaction, as determined by H. Staudinger,[4] can be directed to the formation of the monomeric sulfone by the addition of a polyhydric phenol or to the polysulfone by the addition of a peroxide.



He also has shown that the concentration of the reactants and the nature of the diene employed affect the ratio of monomeric to polymeric sulfone.

Early work by Staudinger[3c] and Eigenberger[3d] demonstrated that the monosulfones decomposed and the decomposition temperature was dependent upon the substituent groups of the diene but no mention was made as to whether these decomposition temperatures were measured at approximately equal decomposition rates.

H. J. Backer[5] and his co-workers have studied many substituted dienes that undergo this addition reaction. In the course of measuring the physical properties of the sulfones they noted the decomposition temperatures of each material. D. Craig[6] has remeasured the decomposition temperature of the sulfones of butadiene, 2-methylbutadiene-1,3, 2,3-dimethylbutadiene-1,3 and 4-methylpentadiene-1,3 at approximately the same decomposition rates.

This work has been carried out to study the equilibrium of the diene sulfur dioxide reaction and to study the decomposition rates of the resulting sulfones.

Experimental

Starting Materials.—Sulfur dioxide was obtained from the Ansul Chemical Company.

Butadiene, 99.8% or better was obtained by decomposing recrystallized butadiene sulfone, removing the sulfur dioxide with a sodium hydroxide solution, drying the gaseous butadiene over Drierite and storing it at −20° in a five-pound cylinder as liquid butadiene, f. p. −108.9°.

The butadiene sulfone used for this work was recrystallized from water and dried in vacuum over calcium chloride, m. p. 63–64°.

The isoprene was obtained by decomposing its sulfone and removing the sulfur dioxide. The resulting material had the following physical properties: b. p. 34.0 ± 0.1°; f. p. −146.6°; d^{20}_4 1.4164.

The isoprene sulfone was recrystallized from water, m. p. 63–64°, solubility 7.85 mg./100 g. of water at 25°.

Piperylene was obtained by decomposing its liquid sulfone, b. p. 40–42°.

Equilibrium Study

Butadiene Sulfone.—Butadiene and the sulfur dioxide were mixed in weighed quantities sufficiently large to make a complete set of experimental determinations and 0.1% *p*-*t*-butylcatechol (based on the weight of the hydrocarbon) was added as an inhibitor. The composition of the mixture was checked by the standard Orsat technique. The reaction mixture, in liquid phase, was poured into glass ampoules of 1.5-ml. capacity. These ampoules were sealed, weighed, then placed in an electrically heated aluminum block capable

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[1] Prepared for the 1945 Meeting-in-Print of the Division of Physical and Inorganic Chemistry, American Chemical Society.

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[3] (a) F. E. Matthews, German Patent 236,386; *Friedländer*, **10**, 1039 (1913); (b) G. de Briun, *Verslag Akad. Wetenschappen*, **23**, 445–446 (1914); *C. A.*, **9**, 634 (1915); (c) H. Staudinger, German Patent 506,839; *C. A.*, **25**, 522 (1913); (d) E. Eigenberger, *J. prakt. Chem.*, **127**, 307–335 (1930).

[4] H. Staudinger, *Ber.*, **68A**, 455–471 (1935).

[5] J. H. Baker, *et al.*, *Rec. trav. chim.*, **51**, 294 (1932); **53**, 524 (1934); **54**, 170 (1935); **54**, 538 (1935); **55**, 898 (1936); **56**, 1063 (1937); **56**, 1069 (1937); **58**, 778 (1939); **59**, 422 (1940); **59**, 890 (1940); **59**, 1141 (1940).

[6] D. Craig, THIS JOURNAL, **65**, 1006 (1943).

of being rocked and controlled at any desired temperature by an L. & N. Controller-Recorder. After the desired reaction time the bombs were removed and immediately chilled in a Dry Ice-bath. The tips of the bombs were broken to allow the unreacted butadiene and sulfur dioxide to evaporate; the resulting crystalline sulfone was then weighed. As a check on the weight of the sulfone, some of the samples were decomposed and the residue weighed. The amount of residue corresponded to the amount of *p*-*t*-butylcatechol added as the inhibitor.

An excess of butadiene is not desirable in the equilibrium studies since butadiene tends to undergo side reactions by forming butadiene polymers which make the analysis more difficult. From the Orsat analysis, the weight of the starting materials and the weight of the butadiene sulfone, the equilibrium constant can be calculated. The results of these experiments appear in Table I.

TABLE I

BUTADIENE SULFONE EQUILIBRIUM (REACTANT SIDE)

T., °C.	Millimoles at Equilibrium Sulfone	C_4H_6	SO_2	*n*	K_n
170	2.07	5.11	10.87	18.05	0.7
160	3.85	6.74	10.10	20.69	1.2
150	5.72	5.50	8.24	19.46	2.5
140	8.07	4.51	6.40	18.98	5.3

Equilibrium was approached also from the butadiene sulfone. Samples of butadiene sulfone were weighed and sealed into 1.5-ml. glass ampoules. These ampoules were then treated in a manner similar to the procedure for preparing butadiene sulfone. The results are shown in Table II, for approaching the equilibrium from the product side.

TABLE II

BUTADIENE SULFONE EQUILIBRIUM (PRODUCT SIDE)

T., °C.	Millimoles at equilibrium Sulfone	C_4H_6	SO_2	*n*	K_n	Av. K_n of several detns.	Av. % dev.	No. of detns.
120	64.45	17.8	17.8	100.0	20.4	18.5	10.4	4
116	24.3	0.74	83.1	104.0	41.0	41.0	2.7	3
100	62.60	0.91	41.5	105.0	175.0	175.0	15.3	9
90	16.87	1.03	1.03	18.9	303.0	304.0	0.2	2

Decomposition Rate Studies of Butadiene Sulfone.—Samples of pure butadiene sulfone were placed in tared, small open mouth tubes. These tubes were heated in a bath at the appropriate temperature. After the reaction time had elapsed, they were removed, cooled and then evacuated until constant weight was obtained. From these data, shown in Table III, the specific decomposition rate was calculated.

TABLE III

DECOMPOSITION RATE STUDIES OF BUTADIENE SULFONE

T., °C.	Time, min.	C_0	C	*k* min.$^{-1}$	Av. *k* min.$^{-1}$ of several detns.	Av. % dev.	No. of detns.
135	50	2.99	0.375	0.042	0.042	9.0	8
125	21	2.39	.118	.014	.015	13.5	5
120	300	3.00	.091	.012	.012	6.7	6
99.5	1440	6.05	4.95	.0014			
91	1290	7.65	4.80	3.7×10^{-4}			
76	8700	11.53	7.88	4.4×10^{-5}			
Room temp.	1982 (days)	10.32	10.23	3×10^{-9}			

Piperylene Sulfone.—The equilibrium data on piperylene sulfone using pure piperylene and sulfur dioxide were not as reliable as those taken on butadiene sulfone because of the difficulty of removing traces of sulfur dioxide from the liquid piperylene sulfone and the tendency for piperylene to form polymers and polysulfones. For these reasons, the piperylene was initially diluted with *n*-pentane to 50 and 25% solutions by weight. These solutions were mixed with sulfur dioxide and the inhibitor in a manner similar to that outlined under butadiene sulfone.

TABLE IV

PIPERYLENE SULFONE EQUILIBRIUM

T., °C.	Millimoles at Equilibrium Sulfone	C_5H_8	SO_2	Pentane	*n*	K_n
			50% Piperylene			
140	1.66	8.01	20.01	9.44	39.12	0.41
120	2.98	6.24	17.84	9.44	36.50	0.98
100	5.38	4.21	15.31	9.44	34.34	2.87
80	7.03	2.06	13.66	9.44	32.19	8.03
			25% Piperylene			
140	1.62	8.08	51.08	28.33	89.11	0.35
120	3.51	6.05	50.15	27.68	87.99	1.02
100	5.92	3.72	49.42	28.33	87.39	2.81
80	7.51	1.51	47.21	28.33	84.56	8.91

Decomposition Rate Studies of Piperylene Sulfone.—A large aliquot sample of piperylene sulfone was first decomposed to determine the amount of polymer and undecomposable material present in the sample. Two runs indicate the purity of the liquid decomposable piperylene sulfone is 81.7 and 82.0%. An average of 81.9% was used to correct the initial weight of piperylene sulfone in the decomposition studies.

A large weighed sample of piperylene sulfone in a tared Erlenmeyer flask was placed in a constant temperature bath at the desired temperature and allowed to remain for a specific time. The flask was removed hot and weighed as rapidly as possible and immediately replaced in the bath. This procedure was repeated several times at each temperature to determine the amount of piperylene sulfone that had been decomposed.

TABLE V

DECOMPOSITION PIPERYLENE SULFONE

T.,[a] °C.	Time, min.	C_0	C	*k* min.$^{-1}$	Av. *k* min.$^{-1}$ of several detns.	Av. % dev.	No. of detns.
94	5	21.67	20.81	0.0081	0.0071	34.3	4
90	10	21.00	19.85	.0056	.0052	12.6	4
85	10	25.91	25.06	.0033	.0033	2.1	4

[a] The temperature is the value obtained by placing a thermometer in the sulfone.

Decomposition Rate Studies of Isoprene Sulfone.—By-products formed during the equilibrium study of isoprene sulfone made the results unreliable; therefore, only the data on the decomposition of recrystallized isoprene sulfones are reported using the technique applied to the piperylene sulfone experiments. The data are presented in Table VI.

TABLE VI

DECOMPOSITION OF ISOPRENE SULFONE

T., °C.	Time, min.	C_0	C	k min.$^{-1}$	Av. k min.$^{-1}$ of several detns.	Av. % dev.	No. of detns
138	10	168.13	86.03	0.067	0.064	30.3	4
130	10	197.33	150.93	.027	.028	18.0	6
120	15	98.13	85.33	.0093	.0093	7.5	6
110	34	150.51	136.61	.0029	.0028	11.0	4
100	12	181.53	179.63	.00091	.00099	25.6	7

Discussion

Sulfone Equilibrium.—The formation of the monosulfone from a diene and sulfur dioxide is a typical equilibrium reaction, dependent upon the concentration of the reactants and the temperature. The reaction of butadiene and sulfur dioxide has been used as an example illustrative of the general class reaction.

$$C_4H_6 + SO_2 \rightleftarrows C_4H_6SO_2$$

Since it is difficult to express the concentrations in moles per liter under reaction conditions, the equilibrium constant, K_n, is expressed in terms of mole fractions.

$$K_n = \frac{\left(\frac{m_{C_4H_6SO_2}}{n}\right)}{\left(\frac{m_{C_4H_6}}{n}\right)\left(\frac{m_{SO_2}}{n}\right)} = \frac{(n)\,(m_{C_4H_6SO_2})}{(m_{C_4H_6})(m_{SO_2})} \qquad (1)$$

n = total number of moles present at equilibrium conditions.

$m_{C_4H_6SO_2}$ = moles of butadiene sulfone present at equilibrium conditions.

The variation of K_n with temperature has been plotted from the equation

$$\ln K_n = \frac{-\Delta H}{RT} + C \qquad (2)$$

and the heat of formation has been calculated from the curves by the equation

$$-\Delta H = \text{slope} \times 2.30 \times 1.99 \qquad (3)$$

The values of K_n for the butadiene sulfone equilibrium reaction are summarized in Table VII. The first portion of the table shows the K_n values by approaching the reaction from the reactant side (butadiene and sulfur dioxide) whereas the last portion of the table shows the value of K_n by approaching the equilibrium from the product side (butadiene sulfone) to which various amounts of sulfur dioxide were added.

TABLE VII

BUTADIENE SULFONE EQUILIBRIUM

T., °C.	Mole ratio $\frac{SO_2}{C_4H_6}$	K_n
170	1	0.67[a]
160	1	1.2[a]
150	1	2.5[a]
140	1	5.3[a]
120	1	18.5[a]
116	112	41.0[b]
116	146	42.7[b]
100	1	128.0[b]
100	46	175.0[b]
100	545	180.0[b]
90	1	304.0[b]

[a] Reactant side. [b] Product side.

These values are plotted in Fig. 1 and from the slope of the curve the heat of formation of butadiene sulfone from butadiene and sulfur dioxide is calculated to be in the order of 26,600 cal./g. mole of heat evolved. Also included in Fig. 1 is the curve for piperylene sulfone taken from the data in Table IV. The heat of formation of piperylene sulfone from piperylene and sulfur dioxide is 14,900 cal./g. mole of heat evolved.

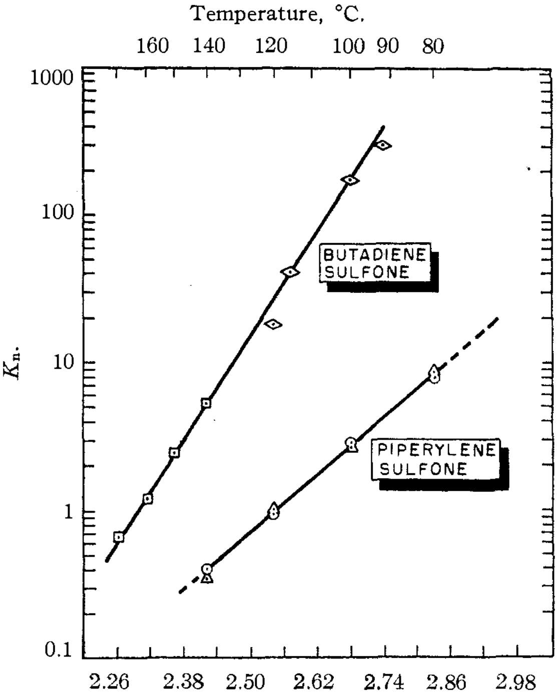

Fig. 1.—Equilibrium constant *vs.* temperature: ⊡, from $C_4H_6SO_2$; ◇, from $C_4H_6 + SO_2$; ⊙, 50% piperylene; △, 25% piperylene.

By measuring the specific decomposition rate at a series of temperatures and plotting this rate against the reciprocal of the absolute temperature the activation energy of decomposition can be obtained from the slope of the line. In Figs. 2 and 3 the plots for the decomposition rates of butadiene and piperylene and isoprene sulfones are shown.

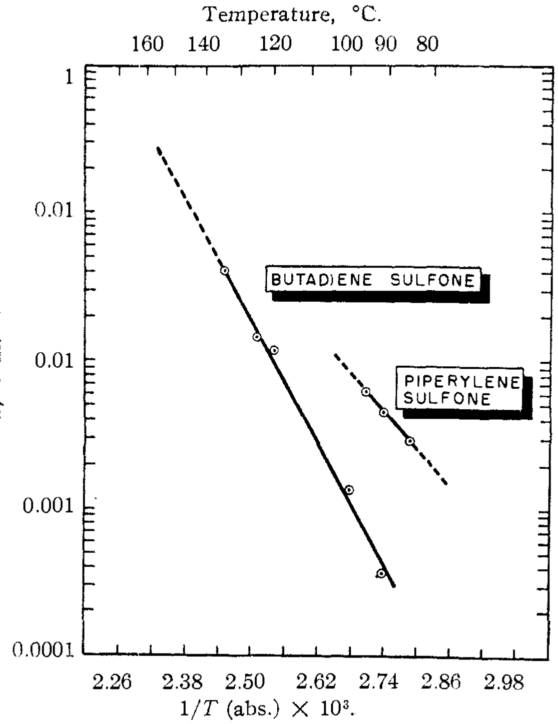

Fig. 2.—Specific reaction rate constant *vs.* temperature.

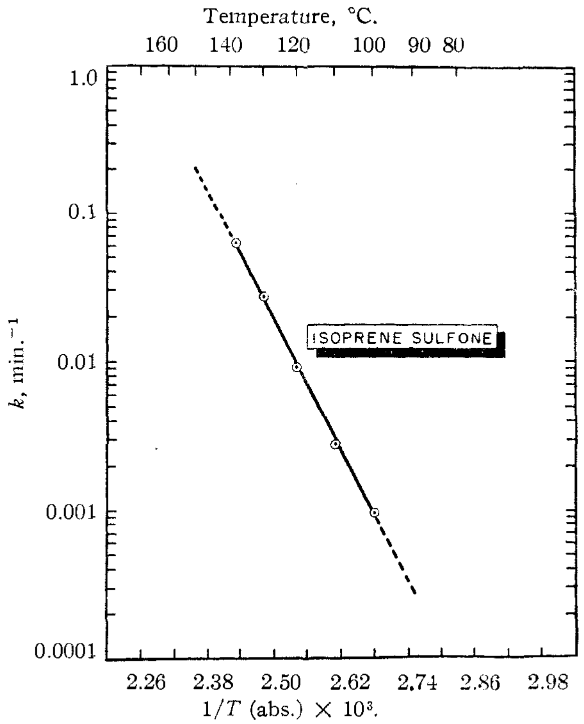

Fig. 3.—Specific reaction rate constant *vs.* temperature.

The calculated heats of formation and activation energy of decomposition for the sulfones of butadiene, piperylene and isoprene are summarized in Table VIII.

TABLE VIII

Monosulfone of	Heat of formation cal./g. mole	Activation energy of decomposition cal./g. mole
Butadiene	−26,600	27,300
Piperylene	−14,900	19,450
Isoprene		32,900

Summary

1. The reaction of a conjugated diene and sulfur dioxide in the presence of an inhibitor to form the monosulfone is an equilibrium reaction.

2. The heats of formation of butadiene sulfone and piperylene sulfone from the diene and sulfur dioxide have been measured and found to be −26,600 and −14,900 cal./g. mole, respectively.

3. The energy of activation for the decomposition of butadiene sulfone, piperylene sulfone and isoprene sulfone have been determined and found to be 27,300, 19,450 and 32,900 cal./g. mole, respectively.

MIDLAND, MICHIGAN RECEIVED[7] AUGUST 12, 1946

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[7] Original manuscript received August 20, 1945.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Thermal Data on Organic Compounds. XXIII. Modern Combustion Data for Fourteen Hydrocarbons and Five Polyhydroxy Alcohols

BY GEORGE S. PARKS, THEO J. WEST, BENJAMIN F. NAYLOR, PAUL S. FUJII AND LESLIE A. MCCLAINE

The accurate determination of the heats of combustion of organic compounds has constituted one of the important lines of experimental work in this Laboratory during the past decade. Four papers,[1] presenting some of the thermochemical results thereby obtained, have already been published. Since 1940 five additional studies within this field have been initiated. Of these, two have been brought to a state of fairly satisfactory completion, while the other three studies have been seriously interrupted by the various wartime activities of the individuals involved. As the resumption of these latter studies is still very uncertain, it now appears desirable to publish briefly our present combustion data, since these are in most cases more reliable than the corresponding data now available in the literature.

Accordingly, we shall here summarize our determinations of the heats of combustion of four-

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[1] Richardson and Parks, THIS JOURNAL, **61**, 3543 (1939); Moore and Parks, *ibid.*, **61**, 2561 (1939); Moore, Renquist and Parks, *ibid.*, **62**, 1505 (1940); Parks and Moore, *J. Chem. Phys.*, **7**, 1066 (1939).