TABLE II

PROPERTIES OF 3,4-DIPHENYLCYCLOPENTADIENONES (VIII, R = C_6H_5)

R_1	R_2	M. p., °C.	Yield, %	Empir. form.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Mol. wt., Calcd.	Mol. wt., Found
CH_3	n-C_3H_7	138[a]	57	$C_{42}H_{40}O_2$	87.5	87.4	6.9	6.9	576	326[d] 356[e]
CH_3	C_6H_5	196[b]	68	$C_{24}H_{18}O$	89.4	89.7	5.6	5.5	322	315[d]
C_2H_5	C_2H_5	103[c]	70	$C_{21}H_{20}O$	87.4	87.6	6.9	7.0	288	282[d]
n-C_3H_7	n-C_3H_7	80[c]	84	$C_{22}H_{24}O$	87.4	88.0	7.6	7.5	316	305[d]
n-C_6H_{13}	n-C_6H_{13}	B. p. 251–255° (4 mm.)	34	$C_{29}H_{36}O$	87.0	86.8	9.0	8.8	400	375[d]

[a] From acetic acid. [b] From butyl alcohol. [c] From ethyl alcohol. [d] In boiling benzene (white solid dimer is 56% dissociated in red solution). [e] In boiling carbon tetrachloride (see ref. 10).

becomes a bright red. After an hour, the dienone is precipitated by water and recrystallized from an appropriate solvent, as a bright red solid. Their properties are collected in Table II.

Cyclopentenolones having long aliphatic chains are purified in a slightly different manner. The crude product (*e.g.*, 2-decyl-3,4-diphenylcyclopentenol-4-one[17]) was taken up in benzene, washed, dried and the solvent removed. The residual oil was distilled; the desired material (23.3 g., 83.5%) is in the fraction, b. p. 200–222° (mostly at 218–220°) at less than 1 mm. It was crystallized from 50 ml. of petroleum ether; the yield was 15 g., m. p. 56–58°, unchanged by further recrystallization.

Anal. Calcd. for $C_{27}H_{34}O_2$: C, 83.1; H, 8.8. Found: C, 83.2; H, 8.7.

Diisobutyl ketone did not condense with benzil under any conditions tried. This appears to be another instance of hindrance to a reaction[18] that is incapable of being forced.

7-Phenoxy-2,3,5,6-tetraphenylindenone (XV).—Benzil and phenoxyacetone were condensed by the usual procedure, and the crude cyclopentenolone after dehydration was at once heated until the thermometer registered 250° at 3 mm. Upon the addition of methanol to the residue, it set to an orange mass of crystals. They were recrystallized from *p*-cymene, or *o*-dichlorobenzene, melted at 308°, and gave the characteristic green color with concentrated sulfuric acid.

Anal. Calcd. for $C_{39}H_{26}O_2$: C, 89.2; H, 4.8; RMgX addn., 1.0. Found: C, 89.2; H, 5.0; addn., 1.1.

Summary

Benzil has been condensed with various aliphatic ketones and the resulting cyclopentenolones dehydrated. The cyclopentadienones so formed may remain as such or dimerize. The limits of the reaction have been outlined.

ROCHESTER 4, N. Y. RECEIVED MAY 5, 1950

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[17] We are indebted to Dr. D. M. Burness, of these Laboratories, for this preparation.

[18] Allen and Rosener, THIS JOURNAL, 49, 2110 (1927).

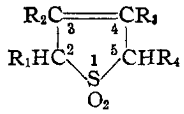
[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

Thermal Dissociation of Methyldihydrothiophene-1-dioxides[1]

BY OLIVER GRUMMITT, ALAN E. ARDIS AND JEAN FICK

Introduction

To study further[2] the thermal stability of the 2,5-dihydrothiophene-1-dioxide or cyclic sulfone ring system, the rates of the thermal dissociation



to the conjugated diene hydrocarbon and sulfur dioxide[3] of several methyl substituted derivatives have been investigated. The compounds reported here are the cyclic sulfones of butadiene (R_1–R_4 are H), of piperylene (R_1 is CH_3, R_2–R_4 are H), of isoprene (R_2 is CH_3, R_1, R_3, R_4 are H), of 1,3-dimethylbutadiene (R_1 and R_3 are CH_3, R_2 and R_4 are H), and of 2,3-dimethylbutadiene (R_2 and R_3 are CH_3, R_1 and R_4 are H).

Experimental

Preparation of Sulfones.—Butadiene (Ohio Chemical) and sulfur dioxide (Ohio Chemical) in a mole ratio of $^1/_2$ and with the addition of 1% of hydroquinone with respect to the butadiene (to retard polysulfone formation)[4] were allowed to react at 100° for 12 hours in a steel bomb[5] or at room temperature for two–three weeks in pressure bottles. The crude sulfone was purified by three crystallizations from hot (50°) water, using Norit in the first crystallization; yields ranged from 80–85%; m. p. 64.5–65.0°.[3b]

Isoprene sulfone was made at room temperature using a 2/1 sulfur dioxide:isoprene mole ratio, 1% of hydroquinone, in 80% yield, m. p. 63.0–63.5°.[3b] Redistilled Eastman Kodak Co. isoprene was used.

Piperylene sulfone was made from Eastman Kodak Co. piperylene which had been isomerized to the *cis–trans* equilibrium mixture according to Frank, *et al.*,[6] and redistilled at 42–43°. Equimolar quantities of hydrocarbon and sulfur dioxide reacted at 100° to give a 50% yield of the sulfone as an oil. This was purified by distilling unreacted hydrocarbon and sulfur dioxide from the crude product, extracting with water, drying and distilling at 0.1 mm.[2a,7]

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[1] Presented before the Organic Division of the American Chemical Society at Atlantic City, September 20, 1949.

[2] (a) Craig, THIS JOURNAL, 65, 1006 (1943); (b) Drake, Stowe and Partansky, *ibid.*, 68, 2521 (1946).

[3] (a) Staudinger, German Patent 506,839; *C. A.*, 25, 522 (1913); (b) Eigenberger, *J. prakt. Chem.*, [2] 127, 307 (1930).

[4] Staudinger and Ritzenthaler, *Ber.*, 68B, 455 (1935).

[5] Hooker, Drake and Stowe, U. S. Patent 2,395,050, Feb. 19, 1946.

[6] Frank, Emmick and Johnson, THIS JOURNAL, 69, 2313 (1947).

[7] We gratefully acknowledge the assistance of Dr. D. Craig of the B. F. Goodrich Company, Research Center, in this vacuum distillation.

This gave a colorless oil, free of polysulfone, as indicated by its complete dissociation at 100°.[8]

1,3-Dimethylbutadiene sulfone, obtained from Shell Development, was crystallized three times from ether; m. p. 40.4–41.0°.[9]

2,3-Dimethylbutadiene sulfone was made at room temperature using a 1/1.5 sulfur dioxide:hydrocarbon mole ratio, 1% of hydroquinone, in 55% yield, m. p. 135–136°.[10] 2,3-Dimethylbutadiene was obtained by dehydration of pinacol.[11]

Rate Measurements.—The reaction vessel was a 10-ml. distilling flask with a side arm 30 cm. long and 5 mm. in diameter, bent near the end and drawn out to a fine opening so that evolved gas was bubbled into two absorption flasks connected in series and each containing 200 ml. of 0.1 *N* sodium hydroxide solution. A gas inlet tube in the neck of the distilling flask allowed the apparatus to be swept out with purified nitrogen before starting the reaction. Sulfite was oxidized to sulfate with hydrogen peroxide, and the excess base back titrated with 0.05 *N* hydrochloric acid.[12] This proved to be more convenient than an iodometric determination of sulfite or a gravimetric determination of barium sulfate. Check analyses on known volumes of pure sulfur dioxide by this method showed an accuracy of 99.0–99.5%. One to two grams of sulfone was taken, the reaction flask was heated in a thermostat controlled to ± 0.02°, and the reaction was allowed to proceed for 15–20 minutes before "zero" time was taken to make certain that the sample had reached the bath temperature.

TABLE I

SPECIFIC REACTION VELOCITY CONSTANTS

Sulfone of	Temp., °C.	Av. *k* min.$^{-1}$ × 10^3	Detns.	Av. % dev.
Butadiene	115.1	6.26	4	2.7
	125.2	16.7	2	1.0
	129.1	24.2	2	1.0
Piperylene	100.0	10.6	2	2.2
	102.0	13.3	1	
	106.3	17.6	1	
	110.5	26.0	1	
Isoprene	108.8	1.35	1	
	115.7	2.81	2	1.6
	125.0	8.70	2	2.4
	135.5	23.6	2	0.5
1,3-Dimethylbutadiene	106.3	8.68	1	
	108.8	12.3	1	
	114.0	22.5	2	0.2
	117.6	29.6	1	
2,3-Dimethylbutadiene	142.7	10.8	2	2.8
	145.2	12.1	1	
	149.2	18.3	2	0.1
	150.8	20.8	2	3.3

Results

The rates of dissociation were followed by measuring the quantities of sulfur dioxide evolved at four to six time intervals from a sample of pure sulfone heated at constant temperature. The reproducibility of the method is shown by the 2.7% average deviation for four experiments run on butadiene sulfone at 115.1° (Table I).

The specific reaction velocity constants were calculated from the slopes of the lines obtained by plotting the log of the sulfone quantity against reaction time. Heats of activation were calculated from the plot of log *k vs.* absolute reaction temperature (Fig. 1, Table II).[13] Entropies and free energies of activation[14] and the frequency factors were calculated at temperatures of equal dissociation rates (Table II).

With the exception of piperylene sulfone, all of the activation energies fall in the range of 32.3 to 35.4 kcal. The low value for piperylene sulfone indicates that the α-methyl group decreases markedly the stability of the sulfone ring. This conclusion is borne out by the differences in heats of formation of butadiene sulfone (−26,600 cal./g. mole) and of piperylene sulfone (−14,900 cal./g. mole).[2b]

The negative entropy value for piperylene sulfone is indicative of a low probability factor for the formation of the activated state. This is usually interpreted as the result of greater rigidity or less randomness in the activated state which in turn would be due to the loss of some degrees of freedom in the transition from normal to

TABLE II

COMPARATIVE DATA FOR THERMAL DISSOCIATIONS OF METHYLDIHYDROTHIOPHENE-1-DIOXIDES

Sulfone of	$H_{act.}$ (kcal./g. mole) This work[a]	Drake, *et al.*[5b]	Temps. for equal dissociation rates (k = 2.64 × 10^{-4} sec.$^{-1}$)	$\Delta S_{act.}$[c]	$\Delta F_{act.}$[d]	Freq.[e] factor
Butadiene	33.6 ± 0.5	27.3	124.7°C.	8.9 ± 1.2	30,100	7 × 10^{14}
Piperylene	24.7 ± .5	19.45	104.7	−10.1 ± 1.3	28,500	5 × 10^{10}
Isoprene	34.6 ± .5	32.9	131.2	9.9 ± 1.2	30,600	1 × 10^{15}
1,3-Dimethylbutadiene	32.3 ± .5	...	110.9	8.6 ± 1.3	29,000	6 × 10^{14}
2,3-Dimethylbutadiene	35.4 ± .5	...	147.6	8.4 ± 1.2	31,900	6 × 10^{14}

[a] These values were calculated by the method of averages (Daniels, "Mathematical Preparation for Physical Chemistry," McGraw–Hill Book Company, New York, N. Y., 1928, p. 235). The errors were estimated by calculating the root mean square errors for the log *k* values and then determining the maximum differences in slopes. [b] The differences in activation energies found by Drake, *et al.*, and here are probably due to the differences in experimental methods. In the earlier work weighed samples were heated in a bath for a given time and the loss in weight noted. This gave a single time interval. Also, the piperylene sulfone used was about 82% pure. [c] In entropy units. [d] In cal./g. mole. [e] In sec.$^{-1}$.

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(8) In a private communication from Dr. R. W. Morse of the Shell Development Company we are informed that intensive purification of this sulfone gave a product which melted at −12°.

(9) Backer, Strating and Kool, *Rec. trav. chim.*, **58**, 778 (1939).

(10) Backer and Bottema, *ibid.*, **51**, 294 (1932).

(11) Kyriakides, THIS JOURNAL, **36**, 992 (1914).

(12) Taylor and Johnstone, *Ind. Eng. Chem., Anal. Ed.*, **1**, 197 (1929).

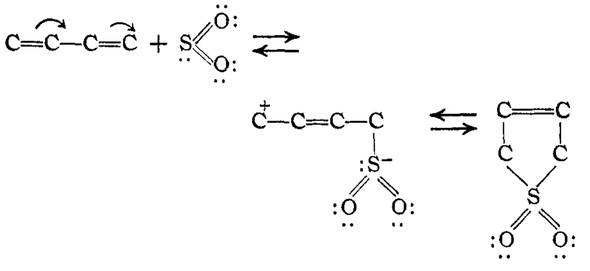
(13) The experimental data and graphs for all the rate measurements are given by A. E. Ardis, Ph.D. Thesis, Western Reserve University, 1948.

(14) (a) Eyring, *J. Chem. Phys.*, **3**, 107 (1935); (b) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw–Hill Book Co., New York, N. Y., 1941, p. 14.

activated state.[15] The significance of this for piperylene sulfone in terms of structure or reaction mechanism is not clear.

The data of Table II also point to a stabilizing effect of a β-methyl group on the sulfone ring, since the heats of activation of the isoprene and 2,3-dimethylbutadiene sulfones, as well as the free energies of activation, are higher than the corresponding figures for butadiene sulfone. A comparison of piperylene and isoprene sulfones and butadiene and 1,3-dimethylbutadiene sulfones show that the stabilizing influence of the β-methyl group is less than the opposing effect exerted by the α-methyl group.

A reasonable explanation for the destabilizing effect of an α-methyl group can be given in terms of an electronic reaction mechanism, if one assumes (a) that the mechanism of 1,4 addition of sulfur dioxide to a conjugated diene is a polar process analogous to the Diels–Alder reaction[16] and (b) that the mechanism of dissociation is the reverse of the addition. Thus the sulfur atom of sulfur dioxide becomes the electron deficient entity as is the ethylene group of maleic anhydride, for example. The electron release (-I) effect of an α-methyl group should facilitate the cleavage of the carbon–sulfur bond in the initial step of this dissociation process.[17] Furthermore, any steric repulsion of the methyl and sulfone groups would favor dissociation.[18]



The interpretation of the stabilizing effect of *beta* methyl substitution is less clear. Analogous properties are shown by certain cyclic anhydrides. For example, dimethylmaleic, tetramethylsuccinic and β,β-dimethylglutaric acids cyclize to anhydrides with remarkable ease.[19] In fact, dimethylmaleic anhydride, which closely resembles the sulfone from 2,3-dimethylbutadiene, forms spontaneously from the acid and the free acid is not known.[20]

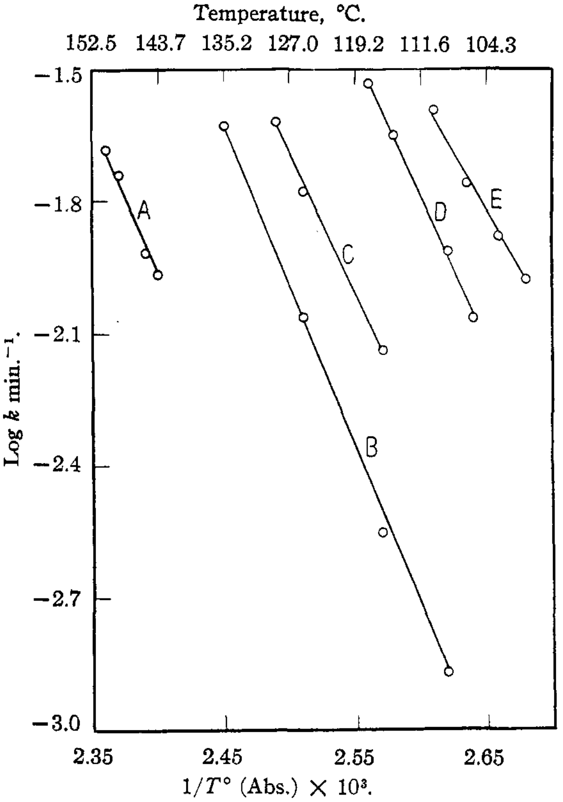


Fig. 1.—Specific reaction rate constants *vs.* temperature: (A) 2,3-dimethylbutadiene sulfone; (B) isoprene sulfone; (C) butadiene sulfone; (D) 1,3-dimethylbutadiene sulfone; (E) piperylene sulfone.

Certain physical properties point to the increased stability resulting from substitution of methyl groups into a ring double bond. For example, the Raman spectra frequencies of the double bond in dialkyl esters and in the anhydrides of maleic, methylmaleic, and dimethylmaleic acids show no change in strain in the case of the esters, which are acyclic, but a marked decrease in strain as methyl groups are introduced in the anhydrides, which are cyclic.[21]

There is no apparent explanation for this behavior in terms of the conventional strain theory or of inductive or electromeric effects.

Summary

A study of the rates of thermal dissociation of the cyclic sulfones of butadiene, piperylene, isoprene, 1,3-dimethylbutadiene, and 2,3-dimethylbutadiene indicates that this reaction

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[15] (a) Ref. 14, pp. 25–27; (b) Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., New York, N. Y., 1946, pp. 1107–1111.

[16] (a) Woodward, THIS JOURNAL, **64**, 3058 (1942); Price, "Reactions at Carbon–Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, p. 49; (b) it is not intended that this mechanism be applied to the photochemical or peroxide-catalyzed reaction of conjugated dienes and sulfur dioxide to give polysulfones. Most likely this is a free radical process.

[17] The kinetics of the dissociation of 1-phenyl-1,3-butadiene sulfone would be especially interesting in the light of this explanation, but this sulfone could not be made from the *cis* or *trans* form of the hydrocarbon (Christoph, Ph.D. Thesis, Western Reserve University, 1949; Grummitt and Christoph, THIS JOURNAL, **71**, 4157 (1949)); Grummitt and Splitter, Organic Division, A.C.S. meeting, Chicago, Sept. 7, 1950.

[18] In this connection, it is interesting to note that only the *trans* isomer of piperylene will readily add sulfur dioxide and dissociation of the sulfone yields only the *trans* isomer.[4]

[19] Wheland, "Advanced Organic Chemistry." John Wiley and Sons, New York, N. Y., 1949, p. 378.

[20] Kettner, *Ann.*, **304**, 156 (799); Fittig, *Ber.*, **39**, 1843 (1906).

[21] Kohlrausch and Skrabal, *Z. Elektrochem.*, **43**, 282 (1937).

(a) is facilitated by α-methyl substitution and (b) is hindered to a smaller degree by β-methyl substitution. A partial explanation for these effects has been given in terms of electronic reaction mechanisms.

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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

The Interaction of Iodine Monochloride with Benzene and Certain of Its Derivatives

BY R. M. KEEFER AND L. J. ANDREWS

Much experimental evidence has accumulated recently which demonstrates that both iodine[1] and bromine[2] interact with aromatic substances, presumably to form 1–1 molecular addition compounds. The equilibrium constants for the formation of a number of such complexes in carbon tetrachloride and *n*-heptane solutions have been evaluated from ultraviolet absorption spectrum measurements.[1b,2b]

The function of the aromatic nucleus in such complex formation appears to be that of an electron donor for the halogen molecule. This is evidenced by the fact that the magnitudes of the equilibrium constants for these reactions are dependent on the electron-release capacities of ring substituents. The equilibrium constant for the reaction of benzene with iodine is somewhat greater than that for the interaction with bromine. These values probably reflect the relative acid strengths (in the Lewis sense) of these two halogens. A polar halogen such as iodine monochloride should function in such reactions as a stronger acid than iodine or bromine. This assumption is confirmed by the results of the present investigation in which, by spectrophotometric procedures, the equilibrium constants for formation of a variety of iodine monochloride aromatic addition compounds have been determined.

Experimental

Materials.—The several aromatic compounds and the carbon tetrachloride were purified as described previously.[2b,3]

Stock solutions (about 0.02 *M*) of iodine monochloride in carbon tetrachloride were prepared by mixing equivalent quantities of carbon tetrachloride solutions of iodine and chlorine.[4] The sodium thiosulfate titer of such solutions remained constant for several days as has been noted[5] with similarly prepared acetic acid solutions of iodine monochloride. The more dilute iodine monochloride solutions required for the equilibrium measurements were prepared by dilution of the stock solution immediately before use.

The Absorption Spectrum Measurements.—Solutions of iodine monochloride in various solvent mixtures of carbon tetrachloride and the aromatic substance under investigation were prepared at 25° and measured on the Beckman model DU spectrophotometer against the solvent mixture as a blank. The cell housing was maintained at 25°. Optical densities ($d = \log_{10} I_0/I = \epsilon lc$ where ϵ = molecular extinction coefficient, l = light path length in cm. and c = concentration of light absorbent in moles/liter) were measured over a wave length range of approximately 280–400 mμ to determine the wave length and intensity of maximum absorption of the complexes. Certain of the solutions were studied in the visible range (up to 560 mμ). All measured optical densities were corrected for the cell blank as determined from measurements in which both cells contained pure carbon tetrachloride. Other details of the method have been described previously.[1b,2b]

Results

The absorption spectra of solutions of iodine monochloride in solvent mixtures of carbon tetrachloride and benzene or substituted benzenes show high intensity maxima in the vicinity of 300 mμ (Table I) very similar to those that have been reported for iodine or bromine in similar solvents.

TABLE I

EXTINCTION COEFFICIENT[a] OF IODINE MONOCHLORIDE IN BENZENE AND SUBSTITUTED BENZENES

Aromatic substance	N_A mole fraction	λ_{max}, mμ	$\epsilon_{max.}$[a]
Benzene	0.956	287	8290
Toluene	.948	294	8090
o-Xylene	.800	303	7050
m-Xylene	.798	301	8340
p-Xylene	.887	295	6860
Chlorobenzene	.825	287	3910
Bromobenzene	.822	289	4350
t-Butylbenzene	.384	290	6330

[a] Molecular extinction coefficients are based on total iodine monochloride present.

If it is assumed, as in the case of the iodine and bromine studies, that the absorption peak in the vicinity of 300 mμ is characteristic of a complex between iodine monochloride and the aromatic substance then the concentration of the complex, (C) is given by

$$\log_{10} I_0/I = d = (C)\epsilon_c l \qquad (1)$$

where d is the optical density at the absorption peak, ϵ_c is the molecular extinction coefficient of the complex and l is the length of the light path in cm. If a 1–1 complex is formed, as represented by the equilibrium

$$\mathrm{ICl} + \mathrm{A} = \mathrm{ICl{\cdot}A} \qquad K = \frac{(\mathrm{ICl{\cdot}A})}{(\mathrm{ICl})(\mathrm{A})} \qquad (2)$$

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[1] (a) Fairbrother, *Nature*, **160**, 87 (1947); *J. Chem. Soc.*, 1051 (1948); (b) Benesi and Hildebrand, THIS JOURNAL, **70**, 2382 (1948); **71**, 2703 (1949); (c) Hildebrand, Benesi and Mower, *ibid.*, **72**, 1017 (1950).

[2] (a) Aickin, Bayliss and Rees, *Proc. Roy. Soc.* (*London*), **124A**, 604 (1929); Bayliss, *Nature*, **163**, 764 (1949); (b) Keefer and Andrews, THIS JOURNAL, **72**, 4677 (1950).

[3] Andrews and Keefer, *ibid.*, **72**, 3113 (1950).

[4] Blair and Yost, *ibid.*, **55**, 4489 (1939).

[5] White and Robertson, *J. Chem. Soc.*, 1509 (1939).