separate binodal curves has been observed in the author's laboratory.[8] These involve liquid carbon dioxide and will be presented in a later paper. They include also several examples of ternary systems with three separate binodal curves on the three sides of the triangular diagrams, a novel phenomenon. Practical uses for some of these systems are shown.

PAULSBORO, N. J.

TABLE II

SYSTEM METHANOL–NITROBENZENE–ISOÖCTANE (WEIGHT PERCENTAGES)

Methanol	Nitrobenzene	Temp., °C.	Methanol	Nitrobenzene
77.0	0	0	8.0	92.0
55.7	17.0		0	85.9
40.3	29.0		(Equil. with solid nitrobenzene)	
27.3	45.5			
25.5	48.2		4.5	0
16.1	60.6		4.7	7.0
5.2	78.1		4.5	8.4
0	86.1		3.8	14.3
			0	12.2
74.2	0	10		
62.1	9.5		5.0	0
40.3	24.5		6.5	3.9
32.1	32.2		7.5	9.7
21.1	42.4		8.7	14.8
16.8	51.0		3.7	17.4
11.8	60.8		0	16.0
4.9	74.0			
0	83.0			
23.5	27.1	14	9.5	8.5
18.0	27.2		12.0	18.2
18.0	32.3		11.3	22.8
14.2	47.0		10.3	24.8
			0	19.5
22.0	27.0	14.1	13.0	20.0
			15.0	25.0
16.0	27.0	Col	16.0	27.0
			12.0	25.0
16.0	30.0		4.0	21.0
72.0	0	15	0	79.7
59.8	9		4.7	70.9
50.9	15.3		12.8	48.3
37.2	22.5		11.8	32.9p.p.[a]
30.8	24.8		10.1	27.7
19.2	21.8p.p.		0	20.2
14.9	20.3			
8.0	6.0			
7.0	0			
69.6	0	20	0	76.2
53.8	9.7		3.7	68.7
46.1	13.9		7.4	57.5
32.0	19.3		7.5	45.5
28.8	20.9		7.0	41.4p.p.
21.9	18.6p.p.		6.4	38.4
9.8	5.8		3.2	28.5
7.5	0		0	23.8
66.6	0	25	0	73.5
52.3	7.9		3.5	60.0
37.7	12.8		3.3	47.9p.p.
24.5	13.4p.p.		0	34.2
14.8	8.9			
11.4	4.9			
8.0	0			
		29.65	0	53.0p.p. (also C.S.T.)
33.6	0p.p. (also C.S.T.)	42.6		

[a] Plait points, P.p.

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(8) A. W. Francis, U. S. Patents 2,631,966 and 2,646,387 (1953).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Diradicals in Solution: Role in Polymerization

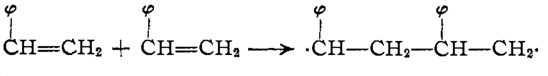
BY K. E. RUSSELL AND A. V. TOBOLSKY

RECEIVED JULY 27, 1953

Diradicals have been produced by the photolysis of 1,4,5-oxadithiacycloheptane. A minimum value for their rate of formation in benzene solution is given by the rate of disappearance of 2,2-diphenylpicrylhydrazyl. In methyl methacrylate the great majority of the diradicals either undergo primary recombination, or form small rings after the addition of one or two monomer units. Few, if any, of the diradicals grow to form long polymer chains. The photolysis of butyl disulfide has been investigated so that comparisons can be made with a disulfide source of monoradicals. The photodecomposition of the *trans*-annular peroxide ascaridole has been shown to lead to monoradicals.

Introduction

For many years it has been considered that the thermal and photopolymerization of styrene proceed by way of diradical intermediates. Flory[1] suggested that initiation of thermal polymerization involves the reaction



$$\overset{\varphi}{\underset{|}{\mathrm{C}}}\mathrm{H{=}CH_2} + \overset{\varphi}{\underset{|}{\mathrm{C}}}\mathrm{H{=}CH_2} \longrightarrow \cdot\overset{\varphi}{\underset{|}{\mathrm{C}}}\mathrm{H{-}CH_2{-}}\overset{\varphi}{\underset{|}{\mathrm{C}}}\mathrm{H{-}CH_2\cdot}$$

and that photopolymerization is initiated by the opening up of the carbon–carbon double bond of a single monomer molecule to give a diradical.

Recently the role of diradicals in these types of polymerization has been questioned.[2,3] It has been shown that if diradicals are formed in the initiation reaction, they are unlikely to grow to long polymer chains but have a high probability of undergoing self-termination to form small rings.[3] In photopolymerization the relationship between the molecular weight of the polymer isolated and the rate of polymerization leads to the conclusion that long chain photopolymer is formed from growing monoradicals[2]; no evidence was found that thermal polymer is formed from growing diradicals.[2]

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(1) P. J. Flory, THIS JOURNAL, **59**, 241 (1937).

(2) D. H. Johnson and A. V. Tobolsky, *ibid.*, **74**, 938 (1952).

(3) B. H. Zimm and J. K. Bragg, *J. Polymer Sci.*, **9**, 476 (1952).

It is clear that new studies are necessary in order to determine the role of diradicals in thermal and photopolymerization. A positive method for the production of diradicals is required so that a technique for following their actual rate of formation can be developed; the method would also allow the direct study of the reactions of diradicals in monomer solution and would give information on the occurrence of ring formation. With such knowledge it is possible to re-examine the problems of thermal and photopolymerization and to shed considerable light on the reactions involved.

Experimental

Methyl methacrylate, from the Rohm and Haas Co., was freed from inhibitor by shaking twice with 5% sodium hydroxide solution, and washed three times with distilled water. It was dried over potassium carbonate, and distilled in an atmosphere of nitrogen at a pressure of 90 mm., a middle fraction with a b.p. range of 0.2° being collected. It was used immediately after distillation.

2,2-Diphenylpicrylhydrazyl was a gift from Dr. R. B. Mesrobian of the Polytechnic Institute of Brooklyn.

***n*-Butyl disulfide** from Eastman Kodak Co. was shaken with lead peroxide and filtered. It was distilled at 3 mm. pressure in an atmosphere of nitrogen.

1,4,5-Oxadithiacycloheptane was obtained from the Thiokol Corporation. It had been prepared by the steam distillation of the disulfide polymer,[4] and distilled at a pressure of 1.5 mm. (b.p. range 64.5–65.5°). It was stored at 0°.

Ascaridole was prepared from wormseed oil (Amend Drug and Chemical Company). The wormseed oil was distilled in an atmosphere of nitrogen at about 3 mm. pressure and a middle fraction collected (b.p. range 76–78°). It was subjected to fractional crystallization and fractional melting three times. The product, m.p. −3°, was stored at 0°.

Ketene was prepared by the method of Hurd and Tallyn.[5] Acetone vapor was passed through a packed quartz tube at 700° and the issuing vapors flowed up a condenser at 20°, where most of the unreacted acetone was condensed out. The ketene was frozen out in a trap at −190°. A bath at −140° was put round the trap and the ketene pumped on for 15 minutes. The trap was then surrounded by a bath at −110° and the ketene distilled off. It was given one distillation *in vacuo*, large end fractions being rejected. It was stored at −190°.

Chloroform, analytical reagent, was obtained from the Mallinckrodt Chemical Co.

Procedure.—Mixtures of methyl methacrylate and either ascaridole or disulfide were placed in 10-mm. Pyrex tubes and, after pumping down to a pressure of 0.5 mm. and degassing, were sealed off. The 60° thermostat in which the reaction tubes were placed had Pyrex walls of thickness less than 2 mm. Irradiations were carried out using a G. E. RS sun lamp as the light source. The significant output is in the range 300–370 mμ, the lower limit being defined by the absorption of the Pyrex glass, and the higher limit by the extinction coefficients of the substances being irradiated. The thermal and photopolymerization of the pure monomer were followed at the same time. The tubes were removed from the bath, rapidly cooled to 20° and the contents washed out with acetone. The polymer was then precipitated in methanol, filtered and dried in a vacuum oven at 60°. In all experiments the monomer conversion was less than 15%.

Molecular weights of polymer samples were obtained by determining intrinsic viscosities in chloroform solution at 20°, and applying the following relation for unfractionated samples[6]

$$\log P_n = 3.261 + 1.256 \log [\eta]$$

2,2-Diphenylpicrylhydrazyl (DPPH) was dissolved in benzene to give a solution of concentration 3×10^{-4} mole/liter. A weighed amount of ascaridole or disulfide was added and irradiations carried out in the presence of air at 60°.[7] The concentration of DPPH was followed by means of a Fisher electrophotometer using a red filter.[7]

The disappearance of cyclic disulfide in monomer solution was investigated by means of its absorption at 320 mμ. Disulfide–monomer mixtures were made up and sealed *in vacuo*, and were irradiated along with samples of pure monomer. The absorption at 320 mμ of the various mixtures before and after polymerization was determined using a Beckman DU spectrophotometer.

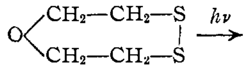
Ketene–monomer mixtures were prepared by adding liquid monomer to a small amount of ketene which had been frozen out in a Pyrex reaction tube. The concentration of ketene was about 0.04 mole/liter, but was not accurately known. The polymerization was followed in the usual way, it being shown that the reactive ketene does not disappear by a rapid direct reaction with methyl methacrylate at 60°. It was found impossible to study the production of methylene radicals in the photolysis of ketene in benzene solution by means of DPPH, because of a rapid thermal reaction between ketene and DPPH.

Results and Discussion

The Photodecomposition of Butyl Disulfide and 1,4,5-Oxadithiacycloheptane.—Solutions of butyl disulfide and 1,4,5-oxadithiacycloheptane in benzene and in methyl methacrylate were irradiated under equivalent conditions. In the wave length region 300–370 mμ the following primary processes should occur

$$\text{(A)}\quad C_4H_9S\text{—}SC_4H_9 \xrightarrow{h\nu} 2C_4H_9S\cdot \text{ (two monoradicals)}$$

(B)



$$\cdot S\text{—}CH_2\text{—}CH_2\text{—}O\text{—}CH_2\text{—}CH_2\text{—}S\cdot \text{ (one diradical)}$$

The primary processes A and B were studied by (a) measuring the rate of disappearance of DPPH in irradiated benzene solutions of the chain and ring disulfides, (b) measuring the rate and degree of polymerization produced in methyl methacrylate by irradiating solutions of the two disulfides in this monomer, (c) measuring the rate of disappearance of the S–S linkage during photolysis of the ring disulfide in methyl methacrylate solution.

(a) Benzene solutions containing DPPH and a disulfide were irradiated, and the rate of disappearance of DPPH was measured. The use of DPPH to count the rate of production of radicals has been established previously.[7–9] A typical curve for the change of concentration of DPPH with time is shown in Fig. 1. In all cases the rate was nearly independent of DPPH concentration over the range $1\text{–}3 \times 10^{-4}$ mole/liter. The results were corrected for the slight amount of fading which occurs when the disulfide is absent. For a concentration of 0.014 mole/liter butyl disulfide and a certain light intensity, the rate of production of radicals as measured by the rate of disappearance of DPPH is given by

$$R_{\mathrm{DPPH}} = 5.6 \times 10^{-8} \text{ mole/liter/second}$$

The result may be affected slightly by the internal filter effect of the DPPH.

The rate of disappearance of DPPH was also measured when benzene solutions of 1,4,5-oxadithiacycloheptane were irradiated. With 0.02 mole/

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[4] F. O. Davis and E. M. Fettes, This Journal, **70**, 2611 (1948).

[5] C. D. Hurd and W. H. Tallyn, *ibid.*, **47**, 1427 (1925).

[6] B. Baysal and A. V. Tobolsky, *J. Polymer Sci.*, **8**, 529 (1952).

[7] C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).

[8] M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, This Journal, **73**, 1700 (1951).

[9] P. D. Bartlett and H. Kwart, *ibid.*, **72**, 1051 (1950).

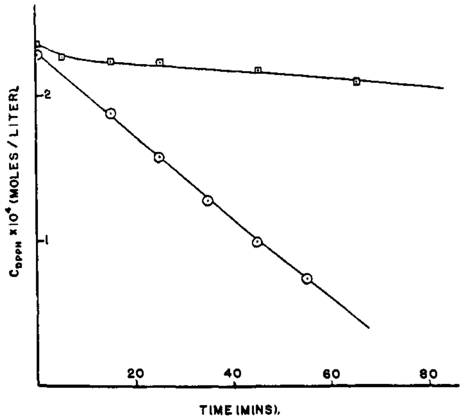


Fig. 1.—Disappearance of DPPH in benzene solution at 60°: ⊙, 0.014 mole/liter butyl disulfide; ⊡, blank run containing no disulfide.

liter of cyclic disulfide and a light intensity approximately the same as that used for butyl disulfide

$$R_{DPPH} = 2.5 \times 10^{-8} \text{ mole/liter/second}$$

Allowing for the difference in concentrations and the greater molar extinction coefficient of the cyclic disulfide as compared with butyl disulfide in the region 300–370 mμ, the DPPH appears to be only about 25% as efficient in reacting with the diradicals formed from 1,4,5-oxadithiacycloheptane as with the monoradicals from butyl disulfide. This assumes that the quantum yields for both disulfides are the same. If the efficiency of the reaction between BuS· and DPPH is unity, as it is for other monoradicals,[9] it is clear that only about one quarter of the diradicals originally formed from the cyclic disulfide react with DPPH. The remainder presumably undergo recombination at a rate which is roughly three times greater than the rate of reaction with DPPH. This is reasonable in view of the ease of formation of 7-membered rings in other reactions.

(b) Rate and degree of polymerization measurements were made on the polymerization of methyl methacrylate induced by the photolysis of butyl disulfide. Values of $1/P_n$, the reciprocal mean degree of polymerization of the polymer, are plotted against R_p (rate of polymerization in moles/liter/second) in Fig. 2, the concentration of the disulfide being 0.014 mole/liter. The rate of polymerization was varied by varying the light intensity. The results in Fig. 2 define essentially the same monoradical line as that determined by Baysal and Tobolsky for the polymerization of methyl methacrylate by the monoradical catalysts 2-azobisisobutyronitrile and benzoyl peroxide.[6]

The rate of initiation of polymer chains R_i in methyl methacrylate at 60° can be obtained from the measured rate of polymerization R_p by means of the relation[6] (assuming no disproportionation)

$$R_i = 1.6R_p^2$$

For a concentration of butyl disulfide of 0.014 mole/liter in methyl methacrylate and a certain light intensity, R_p was equal to 2.7×10^{-4} mole/liter/second, so that R_i was 11.8×10^{-8} mole/liter/second. For the same concentration of butyl disulfide in benzene and approximately the same light intensity, R_{DPPH} was found to be 5.6×10^{-8} mole/liter/second. It is seen that the two independent methods for measuring the rate of production of monoradicals BuS· gave answers in rough agreement considering that no attempts were made for high experimental precision.

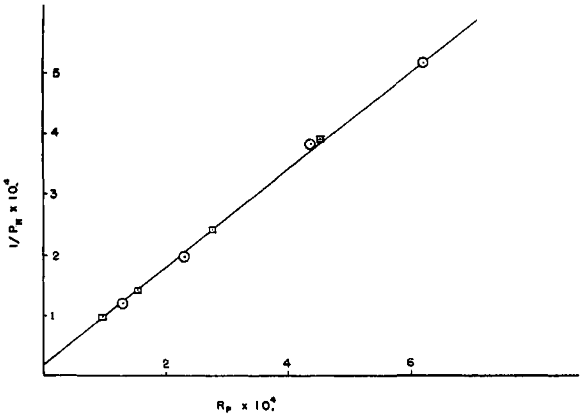


Fig. 2.—$1/P_n$ *vs.* R_p for polymerization of methyl methacrylate at 60°: ⊙, 0.014 mole/liter butyl disulfide; ⊡, 0.014 mole/liter butyl disulfide and 0.027 mole/liter 1,4,5-oxadithiacycloheptane.

Results are also plotted in Fig. 2 for the polymerization of methyl methacrylate containing 0.014 mole/liter of butyl disulfide (the same concentration as used above) and in addition 0.027 mole/liter of 1,4,5-oxadithiacycloheptane. The points on the $1/P_n$ *vs.* R_p curve obtained in this case fall on the same *monoradical* line as those obtained in the presence of butyl disulfide alone, which indicates that transfer to the cyclic disulfide is very slight.

More significant however is the fact that, for a given light intensity, the rates in the presence of butyl disulfide and cyclic disulfide are slightly lower than those obtained with butyl disulfide alone. The photolysis of the cyclic disulfide was therefore not contributing measurably to the initiation of polymer chains in this case. The slight decrease of the rate in the presence of ring disulfide is probably due to an internal filter effect since it absorbs fairly strongly in the region 300–340 mμ.

An apparent absence of initiation of polymer chains was also observed when methyl methacrylate containing 0.027 mole/liter 1,4,5-oxadithiacycloheptane and no butyl disulfide was irradiated. The amount of polymer formed was only 80% of that obtained in a reaction tube containing pure methyl methacrylate irradiated under identical conditions. The cyclic disulfide may exert a slight chemical retardation, but probably the lowering of the polymerization rate in its presence was due to the internal filter effect.

It is striking that under equivalent conditions the efficiency of initiation of long chain polymer by the photolysis of cyclic disulfide in methyl methacrylate is certainly less than 1% of the efficiency of initiation by the chain disulfide. It is possible that no long chain polymer originates from the photolysis of the cyclic disulfide, but there is no decisive evidence on this point. The vast majority of the diradicals formed by the cyclic disulfide in methyl methacrylate suffer one of two fates. They either undergo primary recombination, or they add on one or two monomer units and then combine (or disproportionate). This interpretation emphasizes that ring formation competes with the propagation of polymer chains.[3]

(c) An attempt was made to follow the disappearance of S–S linkages by measuring the ultraviolet absorption of a methyl methacrylate solution of 1,4,5-oxadithiacycloheptane before and after irradiation. A solution of 0.03 mole/liter cyclic disulfide in methyl methacrylate was irradiated for four hours at 60°. The absorption at 320 mμ dropped by 16% of its value, and this is interpreted as a drop in the concentration of disulfide or roughly similar magnitude. Pure methyl methacrylate which was irradiated at the same time gave a slight increase in absorption, so that the decrease observed above is not connected with the conversion of monomer into polymer. Separate experiments showed that the loss of disulfide due to copolymerization with methyl methacrylate was small. The probable conclusion is that some of the diradicals produced by the photolysis of the disulfide react with at least one monomer unit before undergoing ring formation, and thereby convert S–S to S–C linkages.

Photolysis of Ascaridole.—The polymerization of methyl methacrylate at 60° was induced by the photolysis of ascaridole, and the results are recorded in Fig. 3, where $1/P_n$ is plotted against R_p. The results fall on the *monoradical* line, defined by Baysal and Tobolsky[6] for the catalysts benzoyl peroxide and 2-azobisisobutyronitrile.

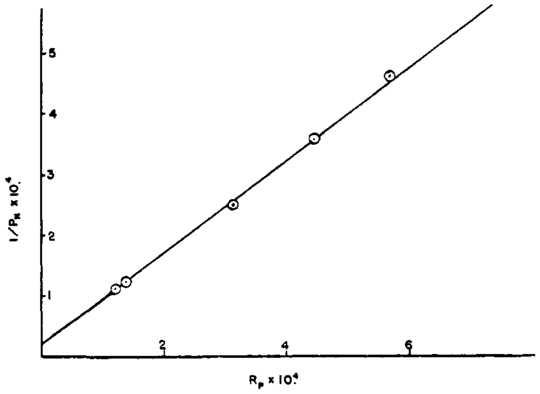


Fig. 3.—$1/P_n$ *vs.* R_p for polymerization of methyl methacrylate at 60°, containing 0.015 mole/liter ascaridole.

The rate of disappearance of DPPH was measured when a benzene solution of ascaridole was irradiated at 30°; the lower temperature was chosen because side reactions complicated the results at 60°. For 0.015 mole/liter ascaridole and a certain light intensity

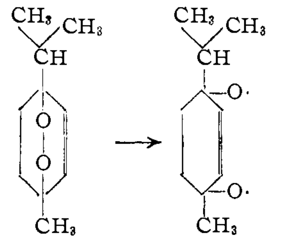
$$R_{\mathrm{DPPH}} = 6 \times 10^{-8} \text{ mole/liter/second}$$

Under approximately the same conditions, the rate of polymerization of methyl methacrylate, R_p = 2.25 × 10^{-4} mole/liter/second at 60°, from which

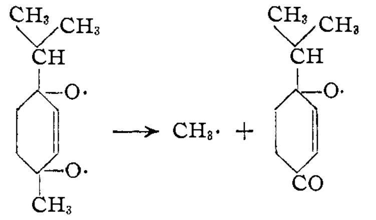
$$R_i = 8 \times 10^{-8} \text{ mole/liter/second}$$

R_i and R_{DPPH} were not measured under exactly the same conditions, but it may be concluded that the two methods of measurement of the rate of production of radicals in the photolysis of ascaridole lead to essentially the same result. The ascaridole results thus compare very well with those obtained in the photolysis of butyl disulfide, and contrast with those obtained using radicals from 1,4,5-oxadithiacycloheptane. The rates of initiation of polymerization by ascaridole and butyl disulfide are in fact very nearly equal in the experiments reported here, though the light absorption by the butyl disulfide in the relevant region is somewhat greater than that of the ascaridole.

The first step in the decomposition of ascaridole is presumably the breaking of the O–O link to give a diradical



This must be followed by a rapid reaction in which two monoradicals are produced, since the radicals are in the form of monoradicals by the time they react with methyl methacrylate or DPPH. By analogy with the decomposition of *t*-butyl peroxide, one possibility is the splitting off of a methyl radical but further evidence on this point is lacking.



The Photodecomposition of Ketene.—The preparation of diradicals from 1,4,5-oxadithiacycloheptane is complicated by the process of primary recombination, and it was thought that the production of radicals by the photolysis of ketene would give a simpler system. The high reactivity of ketene made it difficult to obtain values of R_{DPPH} for the photolysis of ketene solution in benzene. It was shown, however, that irradiated solutions of ketene in methyl methacrylate polymerize at a slightly lower rate than pure methyl methacrylate, a result similar to that obtained with 1,4,5-oxadithiacycloheptane. It is reasonable to conclude that methylene radicals are produced, and that they react with two or three molecules of monomer, but that ring formation prevents the formation of appreciable quantities of long chain polymer.

Further Comments on Diradical Polymerization.—The present work has given no positive evidence for the production of long chain polymer by diradicals in methyl methacrylate. It has not been conclusively proved, however, that all diradicals from 1,4,5-oxadithiacycloheptane undergo self-termination to form small rings in methyl methacrylate, nor can it be inferred that diradicals will not grow to long chain polymer in other systems. In fact, there is some evidence that diradicals from 1,4,5-oxadithiacycloheptane can be the source of polymer of high molecular weight. Photopolymerization of the pure ring compound can be induced by irradiation with ultraviolet light, and if no linear disulfide is present, the reaction presumably proceeds by a diradical mechanism. There is also evidence that, upon irradiation, solutions of 1,4,5-oxadithiacycloheptane in styrene polymerize somewhat more rapidly than pure styrene, in contrast with the results described for methyl methacrylate. An important factor influencing the relative amounts of rings and chains which will be formed in any given case is the steric situation governing ring formation.

Zimm and Bragg[3] have suggested that diradicals produced in thermal polymerization can transfer with monomer to give two monoradicals, and that these monoradicals then grow to give the high polymer observed in the thermal polymerization of styrene. Experimental work with styrene containing substances with high transfer constants does not confirm this suggestion. Mayo, Gregg and Matheson[10] have shown that the addition of 10% carbon tetrachloride to styrene has an effect on the rate which can be explained by the dilution effect. We have measured the rate of polymerization of styrene in the presence of 0.2% *n*-octyl mercaptan and shown that it is a few per cent. less than the rate with pure styrene. Zimm's mechanism would have predicted a considerable increase in rate in both these cases, since the rate of transfer to the carbon tetrachloride or the octyl mercaptan would be far greater than the rate of transfer to monomer.

[10] F. R. Mayo, R. A. Gregg and M. S. Matheson, THIS JOURNAL, **73**, 1691 (1951).

PRINCETON, N. J.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Physical Properties of Organosilicon Compounds. III. Thermodynamic Properties of Octamethylcyclotetrasiloxane

BY ROBERT C. OSTHOFF AND W. T. GRUBB

RECEIVED JULY 30, 1953

The measured vapor pressures of liquid octamethylcyclotetrasiloxane, $[(CH_3)_2SiO]_4$, obey the equation $\log_{10} P_{mm} = 45.7216 - (4530.2/T) - 12.3508 \log_{10} T$. The enthalpy of vaporization, ΔH_v, as a function of absolute temperature may be represented as: $\Delta H_v = 20.7 - 0.0245T$ kcal. mole^{-1}. Activities of $[(CH_3)_2SiO]_4$ in a high molecular weight silicone oil have been determined by measurements of vapor pressure. The polymer–solvent interaction parameter, μ, has a mean value of 0.28 for this system. The constants of Berthelot's equation of state for $[(CH_3)_2SiO]_4$ have been evaluated from approximate values of the critical constants. The true melting point of pure octamethylcyclotetrasiloxane was found to be 17.65°.

Introduction

In a previous study[1] the physical properties of octamethylcyclotetrasiloxane, $\{[(CH_3)_2SiO]_4\}$ (I), have been partially described. In the present paper, the vapor pressure of I has been re-evaluated as a function of temperature and the enthalpy of vaporization has been shown to be strongly temperature-dependent. Since little is known concerning systems containing polydimethylsiloxanes and I, it was of interest to determine the vapor pressures of solution of silicone oil in I and in this fashion to estimate the polymer–solvent interaction parameter.

Experimental

The hydrolysis of dimethyldichlorosilane[2,3] yielded crude I upon distillation. This crude product was then dried over calcium hydride and distilled again, yielding I; n^{20}_D 1.3968; b.p. 175 ± 1°. This product was then further purified by several times partially freezing and discarding the liquid phase.[4] The product resulting from this treatment was frozen and warmed very slowly while measuring the temperature *vs.* time employing a platinum resistance thermometer (calibrated by the National Bureau of Standards) in conjunction with the Leeds and Northrup G-2 Mueller temperature bridge. In this manner the warming curve through the melting range was obtained. An algebraic test of Taylor and Rossini[5] indicated that thermodynamic equilibrium existed between the solid and liquid phase during melting. Employing the usual assumptions that the rate of melting is constant after *ca.* one-half of the sample is melted and that all the impurity exists in the liquid phase, the true melting point of pure I was calculated to be 17.65°.[6,7] The actual melting point of the present sample was found to be 17.58°. Using the freezing point depression constant for I, K_F = 38.0 deg.,[1] a purity of 99.82 mole per cent. was estimated for this material.

A study of the vapor pressure of I as a function of temperature was initiated primarily because the previously reported relation[8] was based upon measurements at only two temperatures. A modified isoteniscope of Smith and Menzies[9,10] was used in the measurement of the vapor pressures using the method previously described[1] for control and measurement of the temperature. A portion of the sample of I (purified as described above) was repeatedly outgassed and finally introduced into the isoteniscope by vacuum distillation. Some observed and calculated values of the vapor pressure of I are presented in Table I.

The constants of equation 1 were determined by application of the method of selected points.

$$\log_{10} P_{mm} = 45.7216 - \frac{4530.2}{T} - 12.3508 \log_{10} T \quad (1)$$

Equation 1 reproduced the observed vapor pressures of liquid I, P_{mm}, with a mean deviation of 0.1 mm. The solution of equation 1 at 760 mm. yielded a value of 176.4° for the normal boiling point (previous value 175.8° at 758 mm.[8]).

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[1] R. C. Osthoff, W. T. Grubb and C. A. Burkhard, THIS JOURNAL, **75**, 2227 (1953).

[2] W. I. Patnode and D. F. Wilcock, *ibid.*, **68**, 358 (1946).

[3] M. J. Hunter, J. F. Hyde, E. L. Warrick and H. J. Fletcher, *ibid.*, **68**, 667 (1946).

[4] F. W. Schwab and E. Wichers, *J. Research Natl. Bur. Standards*, **32**, 253 (1944).

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