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THE REACTION BETWEEN MERCAPTANS AND DIPHENYLPICRYLHYDRAZYL

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The rate of transfer of hydrogen atoms from mercaptans to diphenylpicrylhydrazyl (DPPH) has been investigated at pressures up to 10,000 atm. The reaction is considered as a simple analogue to chain transfer reactions occurring in polymerizing systems, and the results show it to be accelerated about 5-fold at 2700 atm for normal mercaptans, and about 20-fold for tertiary mercaptans.

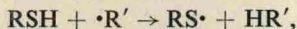
The action of hydrostatic pressure in accelerating liquid-phase vinyl polymerizations has received considerable attention in recent years. The work of Norrish and his collaborators^{1, 2} and of Walling and Pellon³ on styrene in particular has done much to distinguish the effects of pressure on the separate steps of the polymerization process. Most of this knowledge is derived from detailed analysis of the whole process but some steps have also been investigated separately, either directly or by means of analogous simple reactions.

The effect of pressure on the production of free radicals from initiator molecules has been measured directly^{2, 3, 4} and the rate has been found to be retarded between 1.3- and 1.6-fold at 1500 atm.

The addition of an initiating free radical to a monomer molecule can be compared with the iodine-catalyzed isomerization of dichlorethylene in which the rate-determining step is the addition of an iodine atom to the double bond. This reaction has been found to be approximately twice as fast at 3000 atm as at atmospheric pressure.⁵ The rate of the propagation reaction, which has the same mechanism of radical addition to a double bond, has been found to be accelerated six-fold at 3000 atm with styrene.² The large acceleration in this case has been attributed to the ordering effect of pressure on the monomer.

It is usually assumed that the bimolecular transfer reaction is accelerated by pressure to about the same extent as the propagation reaction and this assumption leads to equations^{2, 3} which qualitatively predict the observed change of molecular weight with pressure.

The present investigation was undertaken in order to obtain some direct information about the effect of pressure on transfer reactions by studying a model reaction. The abstraction of a hydrogen atom from a mercaptan,



is a typical transfer reaction which is often used to control polymerization processes. A convenient free radical to use in this reaction is diphenylpicrylhydrazyl (DPPH), as it is stable, easy to handle, and its concentration can readily be measured

optically.⁶ Its solutions in toluene obey Beer's law, showing the substance to be completely dissociated to the free radical; there is therefore no possibility of a "cage effect" in its reactions which might mask the effect of pressure. The reactions between DPPH and *n*-butyl, *n*-hexyl, *t*-butyl, and *t*-octyl mercaptan were studied at temperatures between 25 and 75°C and at pressures up to 10,000 atm.

EXPERIMENTAL

MATERIALS

MERCAPTANS.—The laboratory-grade materials were purified by repeated distillation in an atmosphere of nitrogen and were vacuum-distilled shortly before use. DIPHENYL-PICRYLHYDRAZYL was prepared by the method of Poirier, Kahler and Benington,⁷ the final oxidation to the free radical being carried out with PbO₂ freshly prepared from lead tetra-acetate. The product was recrystallized from benzene + ligroin and dried *in vacuo* at 60°C for several days. TOLUENE (May and Baker laboratory reagent) was repeatedly shaken with concentrated H₂SO₄ and then washed with water and dried over CaCl₂ before being fractionally distilled from Na metal. The final product had a boiling range of less than 0.1 deg.

METHOD

The reactions were carried out as described previously.⁴ All-glass cells were used in a high-pressure spectrophotometer bomb into which paraffin oil was pumped at the desired pressure. The reactions with *n*-butyl, *n*-hexyl, and *t*-octyl mercaptan were followed by measuring optical absorption at 530 mμ while those with *t*-butyl mercaptan were followed at 640 mμ so that greater concentrations of DPPH could be used. Solutions of DPPH in toluene have an absorption peak at 530 mμ with $\epsilon = 1.2 \times 10^4$ (mole⁻¹ l. cm⁻¹), while the reaction products, calculated on the initial concentration of DPPH, have $\epsilon = 444$ (ratio 27.3), at 640 mμ the DPPH solutions have $\epsilon = 4.25 \times 10^3$ and the reaction products $\epsilon = 53$ (ratio 80.2). The observed optical densities were corrected for the relative background absorption of the cells and any change which might occur in this during a run.

The reaction mixtures were made up by weight to be between 0.1 and 0.2×10^{-3} mole kg⁻¹ in DPPH and between 0.2 and 37×10^{-3} mole kg⁻¹ in mercaptan. The toluene was deoxygenated by passing dry, purified nitrogen through it and the solutions were kept free of oxygen by being handled only in an atmosphere of CO₂. Solutions of DPPH in toluene were quite stable at room temperature and faded only very slowly even at the highest temperature and pressure used.

RESULTS

Second-order rate constants were calculated from plots of the logarithm of the optical density against time. As in the work of Russell⁶ the first section of these plots was usually curved indicating an induction period or inhibition by residual oxygen, but the last 40 to 60 % of the reactions gave straight lines from which the slope could be found. The rate of the hydrogen transfer reaction was assumed to be equal to the rate of disappearance of DPPH.

The scatter of the rate constants can be judged from the results obtained with *n*-hexyl mercaptan which are shown in fig. 1. For the other reactions the scatter was somewhat greater and no significance can be attached to the different slopes of the log₁₀ *k* against 1/*T* plots found at different pressures. The activation energies found for the different reactions at various pressures ranged from 12 to 22 kcal mole⁻¹ with a mean of 18 kcal mole⁻¹. Russell found the activation energy of the reaction with five different mercaptans to be 15 kcal mole⁻¹.

Mean values of the second-order rate constants found at different pressures and temperatures for the four mercaptans are summarized in table 1. For two reactions which were taken to 10,000 atm the ratios k_p/k_1 are plotted on a logarithmic scale in fig. 2.

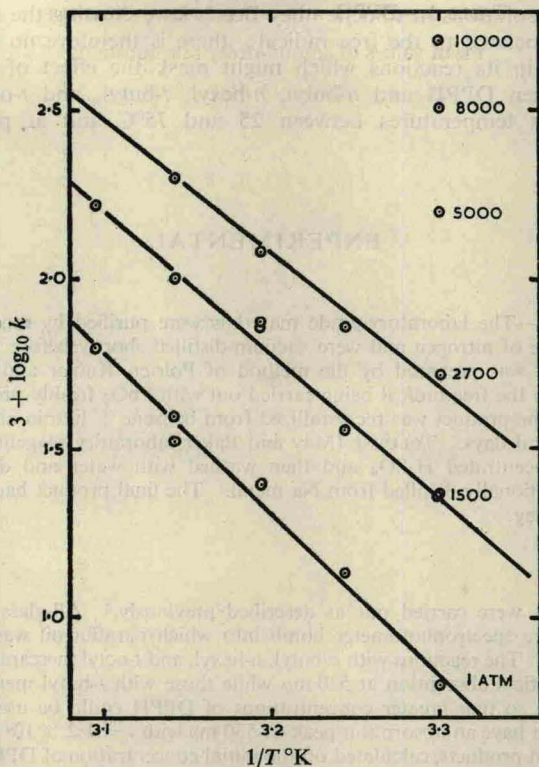


FIG. 1.—DPPH + *n*-hexyl mercaptan in toluene. Change of rate constant with temperature and pressure.

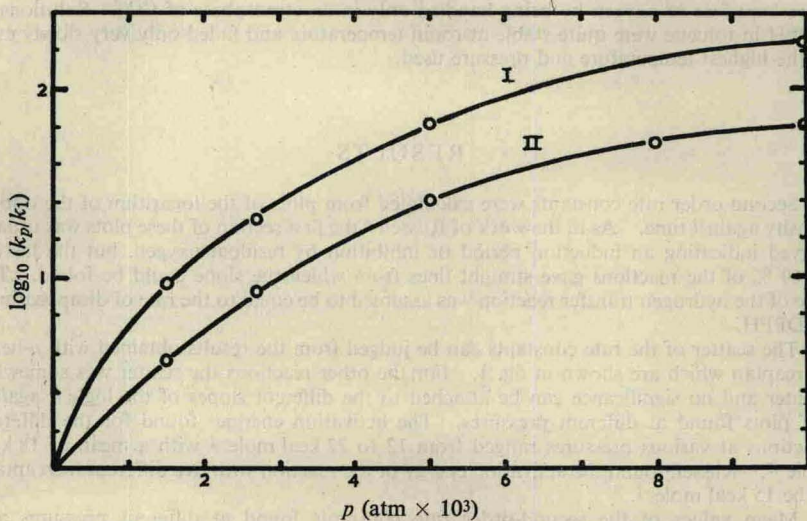


FIG. 2. Effect of pressure on rate of hydrogen transfer. Curve I, *t*-butyl mercaptan + DPPH; curve II, *n*-hexyl mercaptan + DPPH

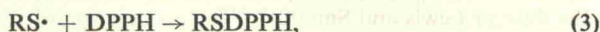
TABLE 1.—DPPH AND MERCAPTAN IN TOLUENE

		mean values of second-order rate constants						
		$k \times 10^3$ (mole ⁻¹ kg sec ⁻¹)						
mercaptan	temp. °C	1	1500	2700	5000	8000	10000	ΔV^\ddagger ml mole ⁻¹ *
		atm						
<i>n</i> -hexyl	30	12.3	46.0	103	316	640	1020	} — 16.8
	35	26.8	71.0	143				
	40	48.6	145	240				
	45	70.4	200	394				
	50	123	326					
<i>n</i> -butyl	35	18.1	35.8	52.0				} — 14.5
	45	33.6	59.0	116				
	55	64.0	134	330				
	75	354	870	2340				
<i>t</i> -butyl	25	0.428	3.94	8.56	27.6		75.2	} — 29.5
	35	0.880	6.62	31.6	77.2			
	45	2.60	14.3	54.0				
<i>t</i> -octyl	35	1.04	1.89	9.52				— 20.7

* ΔV^\ddagger = volume of activation given by $\frac{\Delta \ln k}{\Delta p} = -\frac{\Delta V^\ddagger}{RT}$ with Δp 1 \rightarrow 2700 atm.

DISCUSSION

Although the primary reaction between DPPH and mercaptans appears to be a straightforward hydrogen transfer, the overall rate of disappearance of DPPH is complicated by secondary reactions.^{8a} Russell⁶ assumed that the mercaptyl free radical formed in the primary step reacts with a second molecule of DPPH to form inactive products and that the rate of hydrogen transfer is therefore half the rate of disappearance of DPPH. It has recently been shown, however,⁹ that the overall stoichiometry of the reaction depends both on the nature of the mercaptan and on the relative concentrations of the reagents. The following reaction scheme has been suggested:



where (2) and (3) compete for the mercaptyl free radical formed in (1). A quantitative study showed that between 1.0 and 1.15 mole of DPPH are decolorized per mole of reacting butyl mercaptan and thus (2) appears to be the preferred reaction. For thiophenol the mole ratio ranged from 1 to 2 depending on the relative and absolute concentrations of the reagents. In the present investigation the infra-red spectrum of the reaction products showed that only part of the DPPH was converted to the hydrazine (identified by the N—H band), but no indication of the fate of the remainder of the DPPH could be deduced.

In view of the inhibitory action of the picryl group in some polymerization reactions there could well be some further reaction between HDPPH and RS \cdot formed in (1). By adding HDPPH to the reaction mixture in some kinetic runs and finding the rate constant unchanged, it was, however, shown that such a reaction, if present, does not interfere with either (1) or (3).

From this rather conflicting evidence it appears that the rate constants for

the hydrogen abstraction calculated from the rate of disappearance of DPPH might be uncertain by a factor of two. It is, however, unlikely that there is a complete change of mechanism within the range of conditions used in the present experiments, so that the uncertainty should be rather less when one is comparing rate constants at different pressures and temperatures.

It has been found that DPPH forms fairly stable complexes with benzene¹⁰⁻¹² and this was thought to account for the reaction with *n*-hexyl mercaptan being twice as fast in cyclohexane as in benzene.⁶ We found a similar acceleration of the reaction with *t*-octyl mercaptan on changing the solvent from toluene to hexane or *iso*-octane.

Although the reaction undoubtedly is of a free-radical nature it is strongly affected by the dielectric constant of the solvent. This is illustrated in fig. 3

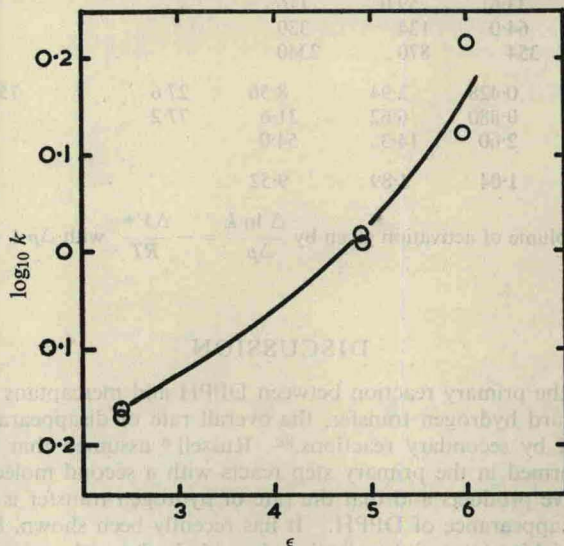


Fig. 3.—Effect of change of dielectric constant on the rate of the *n*-butylmercaptan reaction; 35°C.

which shows the rate constant of the *n*-butyl mercaptan reaction at 1 atm in a mixed solvent as a function of dielectric constant. The solvent was toluene with up to 22 mole % acetonitrile, and its dielectric constant was found by extrapolating the data of Lewis and Smyth.¹³ The acceleration of the reaction with increase in dielectric constant of the solvent indicates that the transition state is more polar than the initial state.¹⁴ As there is evidence from dipole measurements that DPPH is already polarized in solution (dipole moment of 4.92 D),¹⁵ the increase in polarity is probably due to increased polarization of the S—H bond of the mercaptan when this is extended in the transition state. Such enhanced polarization causes an increase in solvation and therefore also an increase in electrostriction of the solvent. This will make a negative contribution to the volume of activation of the reaction and will cause the reaction to be accelerated by pressure.^{16a}

In a purely non-polar bimolecular reaction the volume of the transition state would be expected to be smaller than that of the initial state due to the new bond being partially formed while the old bond is extended only slightly. For the ortho-para hydrogen exchange this contraction has been estimated theoretically^{16b} to amount to 7.7 ml mole⁻¹. For the larger molecules considered here one might expect larger values and on the naive assumption that the contraction in volume

is simply proportional to the cross-section of the hydrogen atom in the one case and to that of the nitrogen atom in the other, one finds a theoretical contraction of 12 ml mole⁻¹. This crude estimate should give a minimum value and shows that the major part of the volumes of activation found experimentally must be due to an actual contraction in the transition state, leaving only a small contribution due to an increase in polarization accompanied by increased electrostriction of the solvent.

The reactions with tertiary mercaptans, although slower at atmospheric pressure, are accelerated much more than those with normal mercaptans. This is in agreement with Perrin's findings¹⁷ that the acceleration of a reaction increases with the complexity of the reacting species.

The rate constants at atmospheric pressure reported in table 1 are in good agreement with Russell's values if one allows for the difference in units and a factor of two in the method of calculation. The rates of reaction of the normal and tertiary mercaptans are in the same order as their efficiencies as chain-transfer agents in vinyl polymerizations. Although the energies of activation of the reactions are approximately the same for all alkyl mercaptans,^{6, 8b} the reactions with tertiary mercaptans appear to have slightly lower entropies of activation. For ionic reactions an approximate proportionality has often been found between entropies and volumes of activation^{18, 16c} and such a relation also seems to apply to the present reactions.

This investigation thus shows that the hydrogen transfer from mercaptans to DPPH is strongly accelerated by pressure: there is a small effect due to the polar nature of the DPPH free radical, but on the whole the reaction appears to be a good model for the transfer reactions in free radical polymerizations. The acceleration found is greater than that postulated for the transfer reaction in styrene² to account for the change in molecular weight of the product with pressure. This may be due to the transfer to monomer in that case not being sufficient to alter the molecular weight of the product significantly.

The author wishes to thank Dr. S. D. Hamann for his continued interest and many helpful discussions and Mr. W. A. Bennett for carrying out some of the measurements.

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² Nicholson and Norrish, *Faraday Soc. Discussions*, 1956, **22**, 104, 97.

³ Walling and Pellon, *J. Amer. Chem. Soc.*, 1957, **79**, 4776, 4786.

⁴ Ewald, *Faraday Soc. Discussions*, 1956, **22**, 138.

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⁸ Walling, *Free Radicals in Solution* (Wiley, N.Y., 1957). (a) p. 527; (b) p. 320.

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¹⁰ Wild, *Faraday Soc. Discussions*, 1952, **12**, 127.

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¹⁴ Ingold, *Structure and Mechanism in Organic Chemistry* (Bell, London, 1953), p. 345.

¹⁵ Turkevich, Oesper and Smyth, *J. Amer. Chem. Soc.*, 1942, **64**, 1179.

¹⁶ Hamann, *Physico-Chemical Effects of Pressure* (Butterworths, London, 1957), (a) p. 163, (b) p. 172, (c) p. 196.

¹⁷ Perrin, *Trans. Faraday Soc.*, 1938, **34**, 144.

¹⁸ Laidler and Chen, *Trans. Faraday Soc.*, 1958, **54**, 1026.

is similar to the one reported in the literature. The rate of reaction is independent of the concentration of the solvent and of the concentration of the other reactants. The rate of reaction is independent of the concentration of the other reactants and shows that the major part of the velocity of addition is due to a reaction which is not accompanied by a significant change in the volume of the reaction mixture. The rate of reaction is independent of the concentration of the other reactants and shows that the major part of the velocity of addition is due to a reaction which is not accompanied by a significant change in the volume of the reaction mixture.

The reactions with tertiary amines, although slower at atmospheric pressure, are accelerated much more than those with normal amines. This is in agreement with Perrin's findings¹⁷ that the acceleration of a reaction increases with the complexity of the reacting species.

The rate constants of atmospheric pressure reported in table 1 are in good agreement with Russell's values¹⁸ and above for the diffusion in air and a factor of two in the region of addition. The rates of reaction of the normal and tertiary amines are in the same order as their diffusivities as chain-transfer agents in vinyl polymerizations. Although the energies of activation of the reactions are approximately the same for all alkyl amines,¹⁹ the reactions with tertiary amines appear to have slightly lower energies of activation. For some reactions an approximate homogeneity has often been found between enthalpy and volume of activation²⁰ and such a relation also seems to apply to the present system.

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