

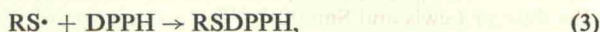
TABLE 1.—DPPH AND MERCAPTAN IN TOLUENE

		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 $\text{RS}\cdot$ 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

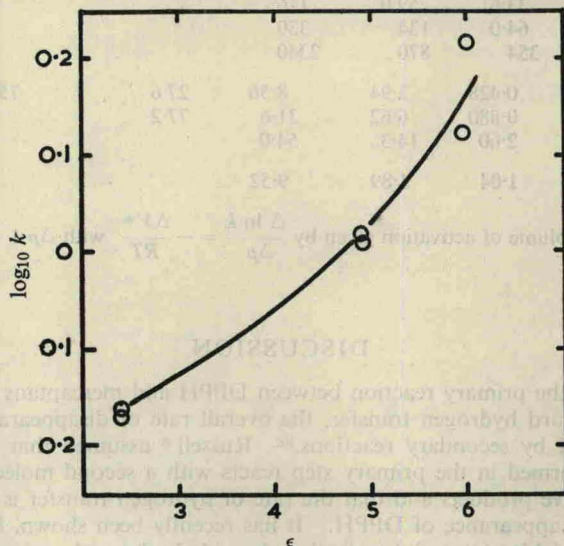


Fig. 3.—Effect of change of dielectric constant on the rate of the *n*-butylmercaptan reaction; 35°C.

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