

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 m μ while those with *t*-butyl mercaptan were followed at 640 m μ so that greater concentrations of DPPH could be used. Solutions of DPPH in toluene have an absorption peak at 530 m μ 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 m μ 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.

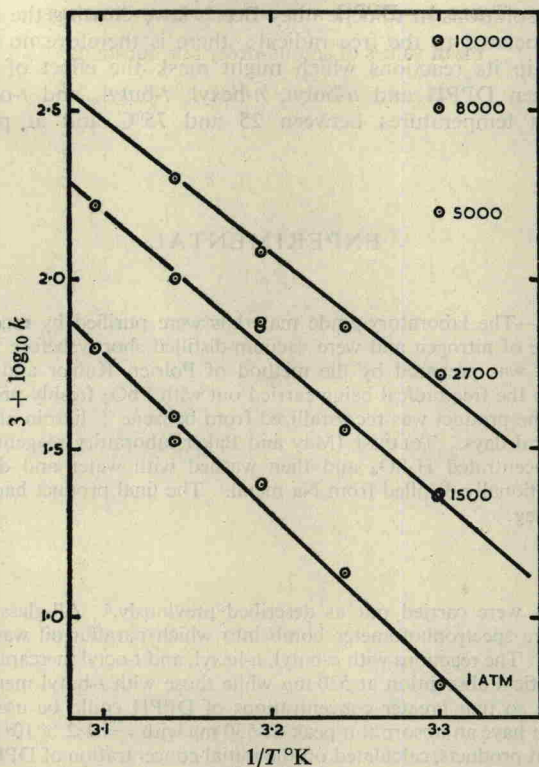


FIG. 1.—DPPH + *n*-hexyl mercaptan in toluene. Change of rate constant with temperature and pressure.

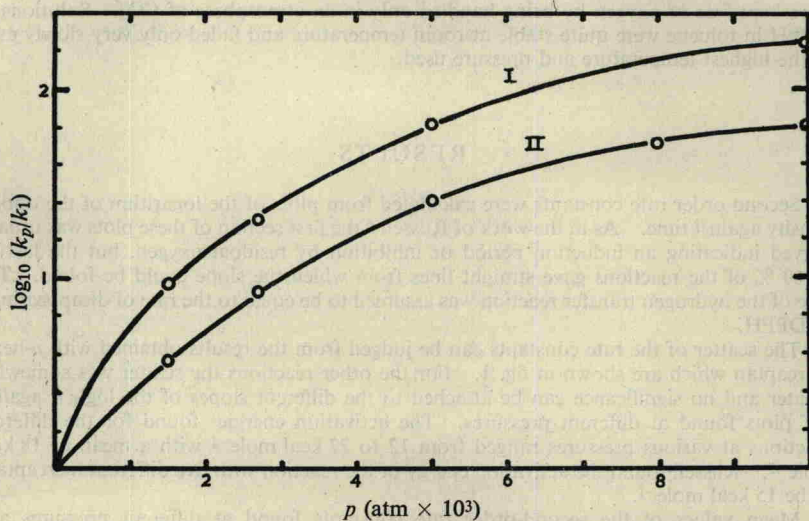


FIG. 2. Effect of pressure on rate of hydrogen transfer. Curve I, *t*-butyl mercaptan + DPPH; curve II, *n*-hexyl mercaptan + DPPH