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 findings [17] 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 styrene [2] 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.

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