# Decomposition and Rearrangement of Free Radicals from Alkyl Phenyl Ethers

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WHEN methyl radicals generated by pyrolysis of di-t-butyl peroxide react with methyl phenyl ether (anisole) in the gaseous phase of 487° K and total pressures of 1—3 cm.Hg, the main products are methane and benzaldehyde, together with smaller amounts of ethyl phenyl ether (phenetole). As indicated in the Figure, the ratio of the rates of production of phenetole ($n_{Pn}$ mole sec.$^{-1}$) and benzaldehyde ($n_{Bd}$), determined in the stirred-flow apparatus described elsewhere,[1,2] is linearly related to the stationary concentration of methyl radicals (calculated from the rate of formation of ethane[2,3]).

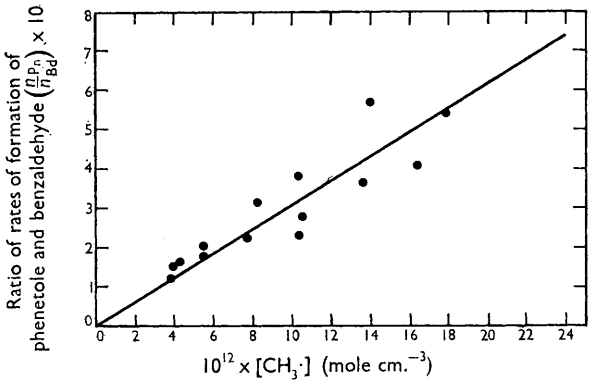


FIGURE. *Dependence of relative rates of formation of phenetole and benzaldehyde on stationary concentration of methyl radicals at* 487°K.

Methane and phenetole are formed by the reactions

$$C_6H_5OCH_3 + CH_3\cdot \rightarrow CH_4 + C_6H_5OCH_2\cdot \quad (1)$$

$$C_6H_5OCH_2\cdot + CH_3\cdot \rightarrow C_6H_5OC_2H_5 \quad (2)$$

Intuitively, benzaldehyde might be expected to result from the following reactions

$$C_6H_5OCH_2\cdot \rightarrow C_6H_5\cdot + HCHO \quad (3)$$

$$CH_3\cdot + HCHO \rightarrow CH_4 + \cdot CHO \quad (4)$$

$$C_6H_5\cdot + \cdot CHO \rightarrow C_6H_5CHO \quad (5)$$

However, (3), (4), and (5), though qualitatively compatible with the presence of traces of hydrogen, carbon monoxide, benzene, toluene, and acetaldehyde in the products, are ruled out by several lines of evidence: (*a*) Kinetic data[4] for reaction (4) combined with the present data would lead one to expect appreciable amounts of formaldehyde in the products. None could be detected, however, by the highly sensitive resorcinol test.[5] (*b*) Since the radical present in highest concentration is the methyl radical, acetaldehyde and toluene should be produced by reactions (6) and (7)

$$CH_3\cdot + \cdot CHO \rightarrow CH_3CHO \quad (6)$$

$$CH_3\cdot + C_6H_5\cdot \rightarrow CH_3C_6H_5 \quad (7)$$

in (at least) comparable amounts to that of the benzaldehyde. This is not the case. (*c*) The production of two molecules of methane for each molecule of benzaldehyde, as required by reactions (1) and (4), is incompatible with the observed stoicheiometry.

It seems that the benzaldehyde is formed by a

[1] M. F. R. Mulcahy and D. J. Williams, *Austral. J. Chem.*, 1961, **14**, 534.
[2] M. F. R. Mulcahy, D. J. Williams, and J. R. Wilmshurst, *Austral. J. Chem.*, 1964, **17**, 1329.
[3] A. Shepp, *J. Chem. Phys.*, 1956, **24**, 939.
[4] A. R. Blake and K. O. Kutschke, *Canad. J. Chem.*, 1959, **37**, 1462.
[5] J. F. Walker, "Formaldehyde", Reinhold, New York, 2nd edn., 1953, p. 370.

combined rearrangement and decomposition of the anisyl radical

$$C_6H_5OCH_2\cdot \rightarrow C_6H_5CHO + H\cdot \qquad (8)$$

This reaction, which is thermochemically equivalent to (3), is compatible with (*a*), (*b*), and (*c*) above. Furthermore, competition between reactions (8) and (2) provides a simple explanation of the results presented in the Figure.

Reaction (8) is further supported by the nature of the products obtained when the reaction is carried out with phenetole or isopropyl phenyl ether in place of anisole. With phenetole, reactions analogous to (3), (4), and (5) would lead to acetophenone

$$C_6H_5O\dot{C}HCH_3 \rightarrow C_6H_5\cdot + CH_3CHO \qquad (3')$$

$$CH_3CHO + CH_3\cdot \rightarrow CH_4 + CH_3\dot{C}O \qquad (4')$$

$$C_6H_5 + CH_3\dot{C}O \rightarrow C_6H_5C(O)CH_3 \qquad (5')$$

Reactions corresponding to (8), on the other hand, would be

$$C_6H_5O\dot{C}HCH_3 \rightarrow C_6H_5C(O)CH_3 + H\cdot \qquad (9)$$

and/or

$$C_6H_5O\dot{C}HCH_3 \rightarrow C_6H_5CHO + CH_3\cdot \qquad (10)$$

(10) being favoured thermochemically. In fact, benzaldehyde alone is formed.

Again, with isopropyl phenyl ether a drastic change in the nature of the main product would be expected on the basis of reaction (3) since the product of the reaction similar to (3) would have no aldehydic hydrogen to be abstracted by a reaction analogous to (4).

$$C_6H_5O\dot{C}(CH_3)_2 \rightarrow C_6H_5\cdot + (CH_3)_2CO \qquad (3'')$$

A reaction similar to (8) and (10), however, would produce acetophenone

$$C_6H_5O\dot{C}(CH_3)_2 \rightarrow C_6H_5C(O)CH_3 + CH_3\cdot \qquad (11)$$

Acetophenone is, in fact, the product.

Thus, reaction (8), although apparently implausible sterically, is supported by a considerable weight of evidence.

The results shown in the Figure lead to the value $3{\cdot}0 \times 10^{10}$ cm.$^3$mole$^{-1}$ for $k_2/k_8$ at 487° K. Combining this with results obtained at 453° K and 540° K and assuming that $k_2$ differs from the rate constant for combination of methyl radicals[3] by virtue only of the effect of the molecular weight of the anisyl radical on the collision frequency, leads to the values $E_8 = 21$ kcal. mole$^{-1}$ and $A_8 \simeq 10^{12}$ sec.$^{-1}$ for the Arrhenius constants of reaction (8) in the pressure range 1—3 cm. Hg. It is remarkable that $E_8$ is close to the value of $\Delta H$ for reaction (8), namely $+ 22 \pm 5$ kcal. mole$^{-1}$.

(*Received, November 1st*, 1965; *Com.* 687.)