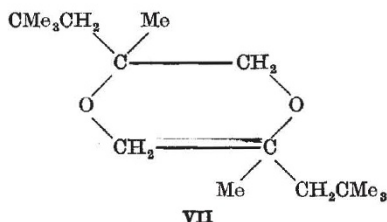


relatively stable isopropyl-type carbonium ion⁵. The subsequent reactions of these intermediate ions depend on the experimental conditions.

1. *Proton Loss*. V may lose a proton either from the methyl or methene group to give the two unsaturated alcohols observed by Hickinbottom, namely, $\text{CMe}_3\text{CH}_2\text{C}(\text{CH}_2\text{OH}) = \text{CH}_2$ and $\text{CMe}_3\text{CH} = \text{CMe}\text{CH}_2\text{OH}$. Only one unsaturated alcohol, as observed, is to be expected from VI, namely, $\text{CMe}_3\text{CHOH.CMe} = \text{CH}_2$.

2. *Anion Addition*. Glycols result from the addition to V and VI of OH^- . In the acetic acid hydrolysis of IV, mentioned by Hickinbottom, the addition of OAc^- will give the 2 acetoxy 3-ol iso-octane.

3. *Condensation with Alcohol or Epoxide*. Ether-type compounds result from the interaction of, for example, VI with IV, yielding the neopentyl substituted 1:4 dioxan (VII), in general conformity with Hickinbottom's observation.



Hickinbottom's work on the iso-octenes throws little light on the double-bond shift sometimes observed in the air oxidation of olefins⁶. The latter is accepted as due to the reaction of the intermediate free radical in its various resonance forms. Hickinbottom's observations, on the other hand, may be ascribed to the formation and subsequent reactions of an isopropyl-type carbonium ion.

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¹ Byers and Hickinbottom, *Nature*, 158, 341 (1946).

² Hickinbottom, *Nature*, 159, 844 (1947).

³ Waters, "The Chemistry of Free Radicals" (Oxford University Press, 1946), p. 245.

⁴ Hammett, "Physical Organic Chemistry" (McGraw-Hill Book Co. Inc., 1940), Chap. 10.

⁵ Evans, A. G., *Nature*, 158, 593 (1946).

⁶ *In. al.*, Bergström, *Nature*, 156, 717 (1945).

DR. BREMNER's suggestions for the mechanism of the formation of unsaturated alcohols from epoxides must await further experimental work to determine the real value of his deductions. In one respect, Dr. Bremner's scheme is doubtful. It might reasonably be expected that the carbonium ions V and VI would lose a proton from the oxygen more readily than from a methyl group, to form carbonyl compounds with or without an alteration in the carbon skeleton.

It has been generally agreed that the free radical hypothesis of the peroxidation of olefins can provide an explanation of the formation of unsaturated hydroperoxides. It has the very serious defect of failing to account for the epoxides and dimeric material which are also formed during autoxidation. The rearrangement of the carbon skeleton which is observed when cyclic olefins undergo autoxidation in acetic acid is a further difficulty. Indeed, the free radical, hypothesis, so far from generally being accepted, is in need of extensive revision.

The object of the suggestion put forward in my note is to provide an alternative hypothesis which, moreover, has the merit of lending itself to experimental investigation.

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Absolute Values of the Rates of Unimolecular Reactions

N. B. SLATER has recently discussed this subject¹. Some time ago, I treated the same problem² not in terms of the normal modes of the molecule, but of the individual bonds where the kinetic energy is expressed as a mixed quadratic form and not as a pure sum of squares. The result, then, seems to permit of an easily visualized interpretation, namely, that the rate constant depends only on the force constant of the breaking bond, the energy required to rupture it, and on the two masses of the atoms adjacent to the breaking bond. It does not depend at all on the remainder of the molecule, which simply acts as a temperature bath. Thus the result is the same as for a diatomic molecule for which the temperature-independent constant is found to be *exactly* equal to its vibrational frequency.

Quantum treatment will slightly modify this² in so far as, especially with light hydrogen atoms, the part of their mass is to be added to the mass of the heavier atom to which they are attached. Thus in a paraffin, a C—C end bond should crack less readily than any of the inner C—C bonds, as the end carbon atoms are more heavily loaded with hydrogen.

Reverting to the classical treatment, it is interesting to note that the temperature-independent factor of the rate constant for a large molecule is in general not equal to one of its proper frequencies, but is equal to the frequency of the imaginary diatomic molecule corresponding to its fissile bond.

I have verified in the case of a linear chain of four equal atoms and equal bonds for motions only along the line joining them, that Slater's result can also be expressed in this simple manner. The conjecture that the rule stated above holds in all cases seems very probable; I have not proved it generally but verified it in many cases.

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¹ Slater, *Nature*, 159, 264 (1947).

² Pelzer, *Z. Elektrochem.*, 39, 608 (1933).

If the internal kinetic and potential energies of the molecule are

$$T' = \frac{1}{2} \sum_1^n \alpha_{rs} \dot{q}_r \dot{q}_s, \quad V = \frac{1}{2} \sum_1^n b_{rs} q_r q_s, \quad (1)$$

and if the oscillations of a particular co-ordinate q_1 (which is to break if it reaches a critical length q_0) are given by

$$q_1 = \sum_1^n \alpha_{s1} \sqrt{\varepsilon_s} \cos(\lambda_s t + \varphi_s),$$