

tively little new material. A census of the first 20 chapters of Part II ("Estimation of the Principal Elements"), making up the alphabetical sequence aluminum to gold, yields an average of a little more than one reference per chapter (24 altogether) dated later than 1959. Purchasers of scientific books have by

this time become hardened to their prices, so that the price of this volume may occasion only mild surprise.

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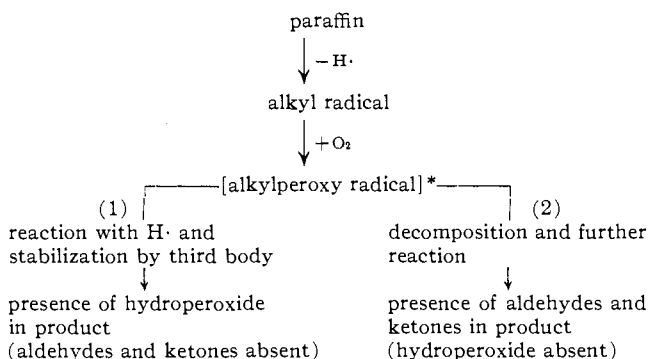
E. B. SANDELL

ADDITIONS AND CORRECTIONS

1950, Volume 72

Elmer J. Badin: The Low Temperature, Low Pressure, Hydrogen Atom Initiated Combustion of Hydrocarbons.

Page 1552. At the end of column 2, replace the simplified reaction mechanism by the following mechanism.

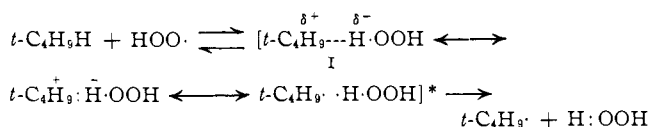


Page 1553. At the end of column 2 before the Summary, the following should be inserted (any part of the paper at variance with the addition should be regarded as having been modified): Only three paraffins (methane, propane, and isobutane) in Table III are unique in that each has a specific type of C-H bond (primary, secondary, or tertiary) at only one carbon. Hence, rates in Table III [see also *J. Am. Chem. Soc.*, **83**, 5045 (1961)] may be used to demonstrate two previously unreported empirical correlations for rate of conversion of paraffin (0.03 ml. STP CH₄ per min., 0.19 ml. STP C₃H₈ per min., and 0.57 ml. STP *i*-C₄H₁₀ per min.) to aldehyde and ketone.

The first empirical correlation is *linearity* of log rate of conversion of paraffin to aldehyde and ketone *vs.* values of C-H bond dissociation energy (CH₃-H, 102 kcal. per mole; *i*-C₃H₇-H, 94 kcal. per mole; *t*-C₄H₉-H, 89 kcal. per mole). Values of bond dissociation energy are those compiled by Cottrell [T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworths, London, England, 1958, pp. 177, 182, 183].

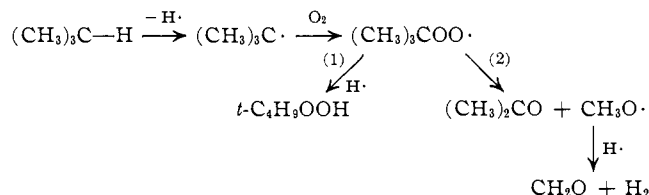
The second empirical correlation is *linearity* of log rate of conversion of paraffin to aldehyde and ketone *vs.* values [R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 619] of the polar substituent constant σ^* (CH₃, 0; *i*-C₃H₇, -0.19; *t*-C₄H₉, -0.30). Inclusion of *n*-butane (rate of conversion is 0.34 ml. STP *n*-C₄H₁₀ per min., σ^* for *sec*-C₄H₉ is -0.21) results in some deviation from the line, the reason probably being that *n*-butane contains secondary C-H bonds at two different carbons.

These correlations suggest there are carbonium ion contributions to the activated complex in the hydrogen-abstraction step, e.g., as in reaction of HOO· radical with isobutane.



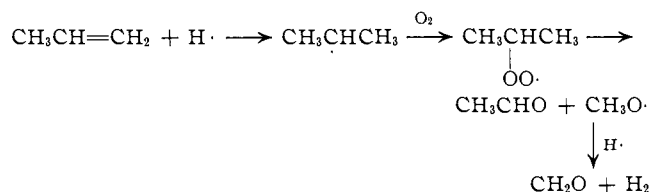
The hypothesis is made that the weakest C-H bond forms a dipole as in I, such a dipole being caused inductomerically by the HOO· radical.

These correlations also suggest that (2) is the main reaction path. The oxidation of isobutane is described below, path 1 functioning to only a minor extent and path 2 functioning to a major extent with formation of about 12 mole % each of acetone and formaldehyde.



This mechanism is somewhat analogous to Semenov's "delayed branching" mechanism as described by Minkoff and Tipper [G. J. Minkoff and C. F. H. Tipper, "Chemistry of Combustion Reactions," Butterworths, London, England, 1962, p. 129] and to the chemical steps suggested by Lewis and von Elbe [B. Lewis and G. von Elbe, "Combustion, Flames and Explosions of Gases," 2nd Ed., Academic Press Inc., New York, N. Y., 1961, p. 174].

Oxidation of olefins under these conditions most probably involves addition of H· followed by further reaction leading to oxidative scission at the double bond.

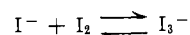


This differs slightly from initial addition of HOO· as suggested by Minkoff and Tipper (p. 173).—ELMER J. BADIN.

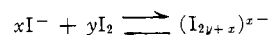
1952, Volume 74

Mansel Davies and Emrys Gwynne: The Iodine-Iodide Interaction.

Page 2748 ff. The title should read "The Iodide-Triiodide Equilibrium in Aqueous Solutions." In addition, the systems



and the further possible equilibria



have been the subject of very many studies in aqueous solutions (L. I. Katzin and E. Gebart, *J. Am. Chem. Soc.*, **77**, 5814, (1955), and references therein). Dr. Ramette of the Chemistry Department, Carlton College, Northfield, Minn., has recently brought to our attention the presence of a number of numerical errors in the Tables I and II of our paper. These errors must be admitted and the senior author (M. D.) must accept the fact that he had not checked all the arithmetical detail.

These details have now been reworked on the same assumptions as previously—in particular, that there is no appreciable variation of K_1 with ionic strength (for which our own specific experiments provide strong support) over the concentrations ranges and for the ionic types relevant to our conditions. The over-all effect of the recalculations is to leave all our previous conclusions unchanged but the new figures show that the uncertainties in K_3 (for equilibrium (1)) extrapolated to zero [I₂] (free iodine concentrations) are larger than previously represented.

Briefly, the revised K_3 values and their estimated uncertainties are:

T, °C.	25	38	49	63
K_3	764.3 ± 2.0	589.0 ± 2.0	500 ± 10	413 ± 2

Thus, for 0.1 M KI at 25° the extreme limits on the extrapolated K_3 give 764.3 ± 2.5 . The over-all best value of ΔH_3 is now