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.

DEPARTMENT OF CHEMISTRY   E. B. SANDELL
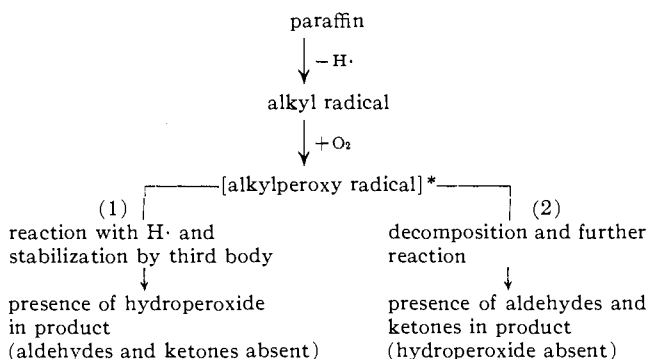UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA   55455

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.

paraffin

$\downarrow -H\cdot$

alkyl radical

$\downarrow +O_2$

[alkylperoxy radical]*

(1) reaction with H· and stabilization by third body

$\downarrow$

presence of hydroperoxide in product (aldehydes and ketones absent)

(2) decomposition and further reaction

$\downarrow$

presence of aldehydes and ketones in product (hydroperoxide absent)
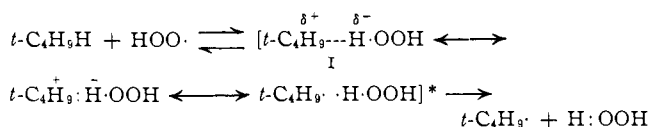
Page 1553. At the end of column 2 before the Summary, the following should be inserted (any part of the paper at variance with the addition should be regarded as having been modified): Only three paraffins (methane, propane, and isobutane) in Table III are unique in that each has a specific type of C–H 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 CH_4 per min., 0.19 ml. STP C_3H_8 per min., and 0.57 ml. STP i-C_4H_{10} 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 (CH_3–H, 102 kcal. per mole; i-C_3H_7–H, 94 kcal. per mole; t-C_4H_9–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].
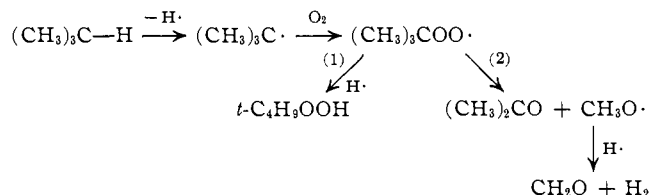
The second empirical correlation is *linearity* of log rate of conversion of paraffin to aldehyde and ketone *vs.* values [R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 619] of the polar substituent constant σ^* (CH_3, 0; i-C_3H_7, −0.19; t-C_4H_9, −0.30). Inclusion of *n*-butane (rate of conversion is 0.34 ml. STP n-C_4H_{10} per min., σ^* for sec-C_4H_9 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.

$$t\text{-}C_4H_9H + HOO\cdot \rightleftharpoons [t\text{-}C_4H_9\overset{\delta^+}{\cdots}H\overset{\delta^-}{\cdot}OOH \longleftrightarrow$$

$$t\text{-}\overset{+}{C_4H_9} : H\cdot OOH \longleftrightarrow t\text{-}C_4H_9\cdot \cdot H\cdot OOH]^* \longrightarrow$$
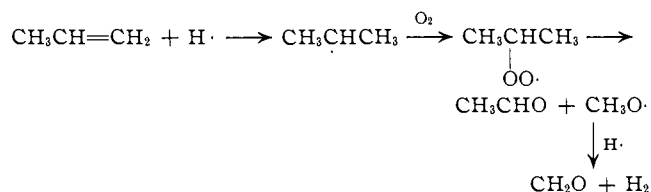
$$t\text{-}C_4H_9\cdot + H : OOH$$

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.

$$(CH_3)_3C\text{--}H \xrightarrow{-H\cdot} (CH_3)_3C\cdot \xrightarrow{O_2} (CH_3)_3COO\cdot$$

(1) ↙ H· \ (2)

t-C_4H_9OOH \qquad $(CH_3)_2CO + CH_3O\cdot$

$\downarrow H\cdot$

$CH_2O + H_2$

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.
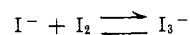
$$CH_3CH{=}CH_2 + H\cdot \longrightarrow CH_3\dot{C}HCH_3 \xrightarrow{O_2} CH_3CHCH_3 \longrightarrow$$

$$\underset{OO\cdot}{|}$$

$$CH_3CHO + CH_3O\cdot$$

$$\downarrow H\cdot$$

$$CH_2O + H_2$$

This differs slightly from initial addition of HOO· as suggested by Minkoff and Tipper (p. 173).—ELMER J. BADIN.
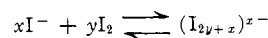
1952, Volume 74

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

$$I^- + I_2 \rightleftharpoons I_3^-$$

and the further possible equilibria

$$xI^- + yI_2 \rightleftharpoons (I_{2y+x})^{x-}$$

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 [I_2] (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

-3316 ± 450 cal. (g.-ion)$^{-1}$, compared with the earlier -3216 ± 400 cal. (g. ion)$^{-1}$. Similarly, from the apparent temperature dependence of ΔH_3, the value of ΔC_p is 34.6 cal. deg.$^{-1}$ (g.-ion)$^{-1}$ (previously, 34.2).

In assessing the *next principal stage* in the further complex ion formation in these solutions it is again found that K_5 (for I_5^-) is markedly varied by changing from 1 M to 0.1 M KI solutions, whereas K_6 (for $I_6{}^{2-}$) remains reasonably constant. A fuller evaluation of ΔH_6 than was previously made does not change its value, -7176 ± 550 cal. (g.-ion)$^{-1}$ (previously, -7150) but with the new ΔH_3 the new $\Delta H_6'$ (for $I_3^- + I_3^- = I_6{}^{2-}$) is -544 cal. (g.-ion)$^{-1}$ rather than -718 cal. (g.-ion)$^{-1}$.

The authors will willingly send further numerical details to those interested, and they wish to thank Dr. Ramette for bringing this matter to their attention.—MANSEL DAVIES.

1956, Volume 78

A. A. Miller and Frank R. Mayo: Oxidation of Unsaturated Compounds. I.

Page 1017. In line 4 of the Abstract, for 38 read 5.

Page 1019. In Table III, the units for the second column should be moles/liter.

Page 1020. Equation 1 should read $d[C_8H_8]/d[O_2]$ etc.

Page 1021. In Fig. 1, the ordinate units are tenths of a mole per liter.

Page 1023. Column 1, paragraph 1, lines 9–16 should read: In the absence of oxygen, the thermal rate at 50° (0.0031 mole/l./hr.)[25] is 0.028 the rate at 0.01 M ADBN (0.11 mole/l./hr.).[12,26] In spite of the low concentration of oxygen at a pressure of 1 atm., the thermal initiation rate in the presence of oxygen is $(0.062/0.028)^2$ or five times the rate in the absence of oxygen. [Reference 25 above was corrected in *J. Am. Chem. Soc.*, **80**, 6697 (1958)].—FRANK R. MAYO.

1957, Volume 79

H. K. Hall, Jr.: Correlation of the Base Strengths of Amines.

Page 5443. In Table I, the sixth entry under primary amines should be isobutylamine instead of n-butylamine.—H. K. HALL, JR.

1960, Volume 82

F. A. L. Anet: The Configuration of Deuterio-L-malic Acid Producted Enzymatically. Synthesis of *threo*-3-Deuterio-DL-malic Acid.

Page 995. In column 2, line 5, change I to II.—F. A. L. ANET.

1962, Volume 84

Calvin M. Lee and W. D. Kumler: Dipole Moments and Structure of Semicyclic Imides.

Page 573. Table IV should read

	Hexa-chloro-butadiene pastes[6]	KBr, 0.5%	CCl₄, 2%	Dioxane, 2%	Benzene, 2%	Heptane, 0.2%
>C=O	1734	1735	1750	1740	1750	1750
	1700	1700	1725	1725	1720	1730
		1650	1700	1700	1700	1700
				1655		1650
			3420	3435	3385	3420
>N—H	3270	3270	3280	3280	3280	3275
	3245	3210	3230	3220	3225	3220
	3190	3150	3175		3175	3165

Column 1, paragraph 1, for the last three sentences read: In CCl₄ and heptane there are bands at 3420 cm.$^{-1}$, due to free >N–H, which increase in intensity on dilution. In dioxane there is a much weaker band at 3435 cm.$^{-1}$. The intensity of the free >N–H band here is probably less, due to most of the molecules hydrogen bonding with the solvent. In benzene there is no band at 3420–3435 cm.$^{-1}$ but one at 3385 cm.$^{-1}$, probably arising from the >N–H hydrogen bonding with the π-system of the benzene. A band at 1650 cm.$^{-1}$ is present in KBr and heptane and one at 1655 cm.$^{-1}$ in CCl₄, which suggest strong hydrogen bond-

ing with the >C=O in these solvents, while no band is present in this region in dioxane and benzene, presumably because of competition for hydrogen bonding by the solvents. This evidence suggests less hydrogen bonding of diacetamide with itself in dioxane and benzene in agreement with the dipole moment data.

Page 575. In Table V: the last column heading should read ($\Delta\nu_{1/2}$ state B)/($\Delta\nu_{1/2}$ state A); wave number 1684 for III, N-methyldiformamide, should read 1694; second line from bottom, second column, 1689 should read 1694; third line from bottom, second column, 0.2% should read 0.1%; tenth line from bottom, second column, 1611 should read 1664.—W. D. KUMLER.

F. A. L. Anet: The N.m.r. Spectra of Cyclic and Acyclic 2,3-Disubstituted Butanes.

Page 749. Column 2, line 7 from bottom, change 2 to $\sqrt{2}$.—F. A. L. ANET.

F. A. L. Anet: The Use of Remote Deuteration for the Determination of Coupling Constants and Conformational Equilibria in Cyclohexane Derivatives.

Page 1054. In Fig. 1, instead of 100 c.p.s., read 90 c.p.s.—F. A. L. ANET.

R. Bruce Martin: Mechanisms of Acid Hydrolysis of Carboxylic Acid Esters and Amides.

Page 4130. The appearance of water as a nucleophile in a pre-equilibrium step is incorrectly treated in this paper. Inferred ω-values do depend upon which step is rate limiting in ester hydrolyses. The discussion given for the γ-butyrolactone enigma is valid only if the first step in ester hydrolysis is rate limiting. Nucleophilic water should not appear explicitly in eq. III-3 and IV-2. The section on values of ω from mechanism should be correspondingly modified. The p term should be deleted from eq. IV-3 and IV-4. Other changes are minor and no general arguments are significantly altered. Two different correct ways for handling nucleophilic water in a pre-equilibrium step are presented in eq. 7 and 11 of a paper by R. Bruce Martin in *J. Phys. Chem.*, **68**, 1369 (1964).

Page 4131. In footnote 4, line 10, for naphthyl read phenyl.—R. BRUCE MARTIN.

1963, Volume 85

K. G. Untch and Robert J. Kurland: The Conformational Equilibration of *cis,cis,cis*-1,4,7-Cyclononatriene; a Determination of Activation Energy and Entropy by N.M.R. II.

Page 347. In column 1, last line, the expression for α is $1 - \Delta^4/\delta^4$ instead of $1 - \Delta^2/\delta^2$.

Page 347. In column 2, first paragraph, the activation energy, $\Delta E\ddagger$, quoted was rather the Arrhenius activation energy, E_a, as defined by the equation $k = A \exp(-E_a/RT)$. Read instead: The Arrhenius activation energy, E_a, as determined from a linear plot of ln k vs. $1/T$ over the temperature range -4.5 to $31.8°$, is 9.69 kcal./mole; the frequency factor, A, is given by log $A = 9.24 \pm 0.02$. The activation parameters, $\Delta E\ddagger$, $\Delta S\ddagger$, and $\Delta A\ddagger$, as defined by the Eyring equation,[7] are 9.12 kcal./mole, -18.2 ± 0.1 cal./°K./mole, and 14.6 ± 0.03 kcal./mole at 27.0°, respectively.

Page 347. In the legend for Fig. 1 read: A, $-40°$; B, $-16.8°$; C, $83.5°$.—K. G. UNTCH.

Adam Allerhand and Paul von R. Schleyer: Solvent Effects in Infrared Spectroscopic Studies of Hydrogen Bonding.

Page 372. Column 2, second line from bottom, for mμ read m.

Page 373. Table IV, the column headed mole % dioxane should read mole % ether. The last three columns headed methanol–dioxane system should read methanol–ether system. Column 2, second line from bottom, for proton donor read proton acceptor.

Page 374. Column 1, fifth line from top, for proton donor read proton acceptor.

Page 376. Figure 5a, the ordinate should read $[(\epsilon - 1)/(2\epsilon + 1)] \times 10^2$. Equation 5 should read $(\nu^0 - \nu^s)/\nu^0 = aG$.

Page 379. Column 2, 16th line from bottom, ..OC(CH₃)₂ should read ..OS(CH₃)₂.—PAUL SCHLEYER.