at pH 5 to completely liberate the products of the acetylene reactions or was fully basified at $<25°$ to liberate basic products.

UNION CARBIDE RESEARCH INSTITUTE   ROBERT S. NEALE
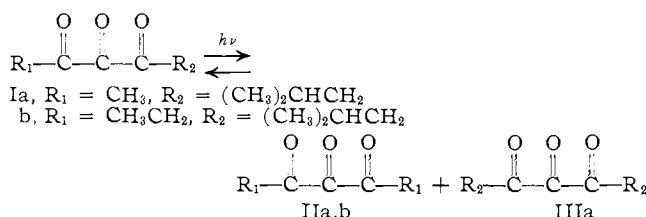TARRYTOWN, NEW YORK

Acyl Exchange Reactions of Vicinal Triones

Sir:

The irradiation of these triones induces the acyl exchange reaction

Ia, $R_1 = CH_3$, $R_2 = (CH_3)_2CHCH_2$
b, $R_1 = CH_3CH_2$, $R_2 = (CH_3)_2CHCH_2$

IIa,b   IIIa

6-Methyl-2,3,4-heptanetrione (Ia)[1,2] (18.33 g., 0.117

mole, bis-2,4-dinitrophenylhydrazone,[2] m.p. 233°) in ether (500 ml.) was swept with helium in a vacuum-line photochemical apparatus attached through condensers (water and Dry Ice) and a manostat (715 mm. maintained) to an automatic pump. The solution was irradiated at reflux with a G.E. sunlamp. Successive analyses (Table II) show that IIa and IIIa are formed, and photoequilibrium is attained. Carbon monoxide (0.005 mole) is evolved. This reaction is photochemical rather than thermal (Ia unchanged after 3 days at 105° in a sealed tube).

Distillation gave IIa[2] (3.21 g., 0.028 mole), Ia[2] (6.53 g., 0.042 mole), IIIa[2] (4.57 g., 0.023 mole), and a residue (2.57 g., two-peak chromatogram). 2,3-Butanedione (0.11 g., 0.0013 mole, H^1 n.m.r. in DCCl3: methyl singlet at δ 2.08; p-nitrophenylhydrazone, m.p. 230°) and acetic acid (0.04 g.) were isolated from the trap condensate. With periodic acid, Ia gave carbon dioxide, acetic acid (p-toluidide m.p. 147°), and 3-methylbutanoic acid (p-phenylphenacyl ester m.p. 78°); and IIIa gave carbon dioxide and 3-methylbutanoic acid (p-toluidide m.p. 107°).

TABLE I
PHYSICAL PROPERTIES[a]

Trione	B.p., °C. (mm.)	$n^{25}D$	Infrared, cm.$^{-1}$	λ_{max} mμ (ϵ)	H^1 n.m.r. spectra[b] R₁——CO——CO——CO——R₃	
Ia	54 (5)	1.4292	1724	220 (447) 464 (27.5)	3 H, δ 2.35 (a).	6 H, δ 0.98 (d), $J = 7.2$; 1 H, δ 2.00 (m); 2 H, δ 2.56 (d), $J = 6.6$
IIa	44–46 (12)		1722	464	δ 2.38 (s); hydrate, δ 2.20 (s)	
IIIa	61–62 (2)	1.4366	1720	220 (1207) 468 (28.6)	12 H, δ 0.98 (d), $J = 7.2$; 2 H, δ 2.00 (m); 4 H, δ 2.57 (d), $J = 6.0$	
Ib	40–42 (2)		1720	464	3 H, δ 1.15 (t); 2 H, δ 2.76 (q), $J = 6.6$.	6 H, δ 0.99 (d), $J = 6.0$; 1 H, δ 2.25 (m); 2 H, δ 2.57 (d), $J = 6.0$
IIb	34–35 (2)	1.4301	1720	462	6 H, δ 1.15 (t); 4 H, δ 2.76 (q), $J = 6.6$	

[a] Those of products and authentic triones identical.   [b] In CCl4 with TMS.

TABLE II
PHOTOCHEMICAL REACTIONS OF Ia AND OF AN EQUIMOLAR MIXTURE OF IIb AND IIIa[a]

Reaction time, hr.	Ia[b]	IIa[b]	IIIa[b]
0	100		
18	81	10	9
30	79	10	10
50	70	14	16
74	58	23	19
116	60	19	20
141	58	19	23
	Ib[b]	IIb[b]	IIIa
0		50	50
1	2	49	49
2.5	8	46	46
4	16	42	42
9	22	39	39
22	32	35	33
45	34	33	33

[a] Mole % (± 2) of each trione. Analyses with Aerograph A-700 5 ft. $\times$ 1/4 in. column with 30% SE 30 on 45/60 Chromosorb B, isothermal 164°, He flow rate 1.04 ml./min.   [b] Retention times: Ia, 2.38 min.; IIa, 1.00 min.; IIIa, 6.50 min.; Ib, 3.63 min.; and IIb, 2.00 min.

Similar results are obtained when IIb[2] (2.25 g., 0.0158 mole, bis-2,4-dinitrophenylhydrazone[2] m.p. 294°) and IIIa (3.11 g., 0.0157 mole) in ether (100 ml., nitrogen swept) are irradiated as before. Sequential analysis (Table II) shows the rapid formation of 2-methyl-4,5,6-octanetrione Ib, and equimolar amounts of Ib, IIb, and IIIa are present at photoequilibrium. Distillation gave IIb (1.41 g., 0.099 mole), Ib[2] (1.62 g., 0.095 mole), IIIa (2.12 g., 0.110 mole), and a residue (0.82 g.).

Acyl exchange occurs as solutions of triones in aldehydes stand in air, or are heated in the presence of peroxides. Ia (25 mole %) in 3-methylbutanal in a foil-covered container with air in the vapor space (10 ml.) gives IIIa (molar ratio of Ia:IIIa after 2 hr. 9:2, and after 48 hr. 7:2). Other products (v.p.c.) are 3-methylbutanoic acid, 2,7-dimethyl-4,5-octanedione, 2,3,4-pentanetrione, and acetic acid. A solution containing Ia (3.9 g., 0.025 mole), 3-methylbutanal (6.6 g., 0.077 mole), and 2,2-bis-(t-butylperoxy)butane (0.3 g.) at 100° under nitrogen in the dark gives IIIa (IIIa:Ia: 1 hr. 0.35; 5 hr. 0.55; 18 hr. 0.90; and 29 hr. 1.4), 2,3,4-pentanetrione, 2,7-dimethyl-4,5-octanedione, and peroxide-derived products (v.p.c.).

This evidence suggests a free-radical chain reaction.

Initiation involves formation of acyl radicals by

(1) All triones (Table I) were prepared according to F. Sachs and A. Rohmer [*Ber.*, **35**, 3310 (1910)] except that their solutions were protected from light, and dioxane and dichloromethane were the solvents used. Ia prepared in room light with ethanol and ether contained 5% IIa, 5% IIIa, and trione ethanolates. Its purification was difficult.
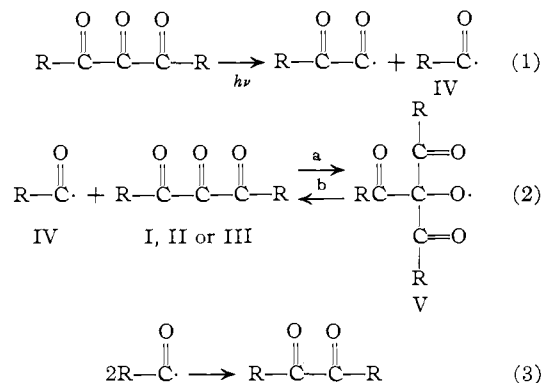
(2) Acceptable analyses obtained.

$$R-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-R \xrightarrow{h\nu} R-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}\cdot + R-\overset{\overset{O}{\|}}{C}\cdot \quad (1)$$
$$\text{IV}$$

$$R-\overset{\overset{O}{\|}}{C}\cdot + R-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-R \underset{b}{\overset{a}{\rightleftarrows}} R\overset{\overset{O}{\|}}{C}-\overset{\overset{\overset{C=O}{|}}{R}}{\underset{\overset{\underset{R}{|}}{C=O}}{C}}-O\cdot \quad (2)$$
$$\text{IV} \qquad \text{I, II or III} \qquad\qquad\qquad \text{V}$$

$$2R-\overset{\overset{O}{\|}}{C}\cdot \longrightarrow R-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-R \quad (3)$$

reaction 1, or by interactions of aldehydes with oxygen or peroxides. Chain propagation is represented by reactions 2a and 2b to emphasize its simplicity. Versions of reactions 2 here involve two acyl radicals IV and three triones. Exchange is effected when reactant IV in 2a is different than the product IV from the succeeding 2b. Reaction 2 is an example of an unusual radical transfer process[3] that involves attack upon an internal atom in a molecule and expulsion of a fragment of it. Since triones are the major products, V must be the dominant intermediate or transition state. The small amount of biacetyl from the photolysis of Ia suggests the chain termination reaction 3.

The above equilibria differ from random distribution (Ia,b:IIa,b:IIIa, 2:1:1). Reaction 2b is not expected to be random since small structural differences profoundly affect the fragmentation of t-alkoxy radicals.[4]

Similar reactions occur with 1,2-diones. Peroxide- and light-induced reactions of 2,3-butanedione with butanal give some 2,3-hexanedione. Study is continuing to determine if the higher boiling products from photolysis of triones are the hydroxycycloalkanediones anticipated from the photolyses of 1,2-diones to give 2-hydroxycyclobutanones.[5]

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(4) (a) F. D. Greene, *et al.*, *J. Org. Chem.*, **28**, 55 (1963); (b) C. Walling and A. Padua, *J. Am. Chem. Soc.*, **85**, 1593 (1963).

(5) (a) W. H. Urry and D. J. Trecker, *ibid.*, **84**, 118 (1962); (b) W. H. Urry, D. J. Trecker, and D. A. Winey, *Tetrahedron Letters*, **14**, 609 (1962).

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Spectrophotometric Detection of Hydrated Electrons in Co⁶⁰ γ-Ray Irradiated Solutions[1]

Sir:

In the present letter, we demonstrate the feasibility of direct spectrophotometric determination of e_{aq}^- in Co⁶⁰ γ-ray irradiated solutions. Heretofore, hydrated electrons, e_{aq}^-, have been directly observed only during pulse radiolysis.[2,3] Extensive use has been made of the intense optical absorption spectrum of the hydrated
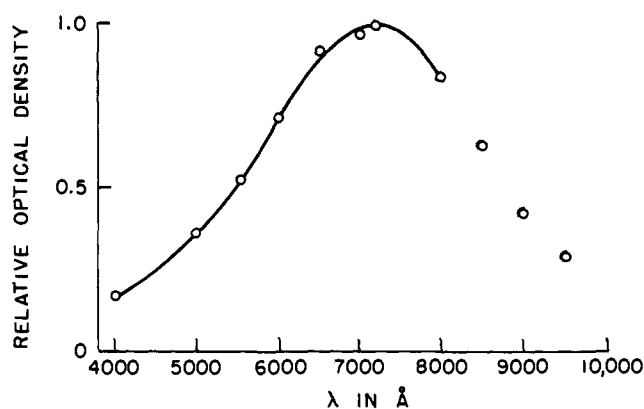
Fig. 1.—Spectrum of the hydrated electron: solid line, pulse radiolysis method, Keene[3]; circles, present work.

electron to measure absolute rate constants and to demonstrate its formation from hydrogen atoms and photochemically from negative ions.[4] In the past, such studies have required the use of a linear accelerator but now it is possible to expand work on e_{aq}^- to laboratories having Co⁶⁰ γ-ray or X-ray sources capable of delivering up to 500–1000 rads/sec. available.

The steady-state concentration of hydrated electrons has been measured in Co⁶⁰ γ-ray irradiated water. We find that the optical density of a 0.001 N sodium hydroxide solution saturated with hydrogen increases perceptibly at 7200 Å. upon exposure to γ-rays. The absorption disappears upon removal of the γ-ray source. By measuring the intensity of absorption in the region from 4000 to 9000 Å., we obtain an absorption spectrum identical with that found in the pulse radiolysis of water[2] (see Fig. 1). When the solution is acidified, no transient absorption is found at 7200 Å. Thus we conclude that this transient species is the hydrated electron.

A water-jacketed, cylindrical irradiation cell, 1 cm. in diameter and 40 cm. in length, provided with supersil end windows, was irradiated in a shielded cave in the chemistry hot laboratory by a 40-cm. long 15,000 c. Co⁶⁰ source. Fluctuations in optical density were minimized by flowing water at constant temperature through the jacket of the cell. The optical absorption of the solution was measured by light from a tungsten filament lamp that passed through the cell into a F 3.5 monochromator and at selected wave lengths into a photocell. Maximum optical density changes of 0.0082 were found at 7200 Å. Under our conditions of irradiation, this optical density change corresponds to an e_{aq}^- concentration of 1.4×10^{-8} M.

A hydrogen-saturated alkaline solution is an excellent one for studying reactions involving e_{aq}^-. At pH 11, all H atoms and OH radicals formed during irradiation are converted to e_{aq}^- by the following reactions.

$$H + OH^- \longrightarrow e_{aq}^- \quad (1)$$
$$OH + H_2 \longrightarrow H + H_2O \quad (2)$$
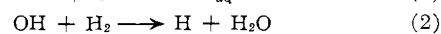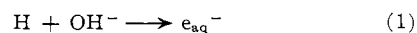
The disappearance of e_{aq}^- is primarily by the second-order reaction

$$e_{aq}^- + e_{aq}^- \longrightarrow H_2 + 2OH^- \quad (3)$$
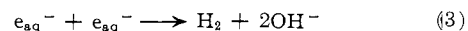
since the first-order reaction

$$e_{aq}^- + H_2O \longrightarrow H + OH^- \quad (4)$$