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CATALYSIS OF LIGHT INITIATED DECARBONYLATION OF ALDEHYDES[1]

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THE decarbonylation of certain aliphatic aldehydes proceeds by a free radical chain reaction which can be initiated by di-t-butyl peroxide[2,3] at 130-140° and by ultraviolet light.[4,5] Radicals from dimethyl 2,2'-azoisobutyrate were rather ineffective, but addition of a small quantity of benzyl mercaptan led to extensive decarbonylation of α-branched aldehydes.[6] The peroxide catalyzed decarbonylation may be described by equations (1-3).

$$I\cdot + RCH=O \longrightarrow IH + R\dot{C}=O \qquad (1)$$

$$R\dot{C}=O \longrightarrow R\cdot + CO \qquad (2)$$

$$R\cdot + RCH=O \longrightarrow RH + R\dot{C}=O \qquad (3)$$

The mercaptan assisted process may involve the following reactions:

$$I\cdot + R'SH \longrightarrow IH + R'S\cdot \qquad (4)$$

$$R'S\cdot + RCH=O \longrightarrow R'SH + R\dot{C}=O \qquad (5)$$

$$R\dot{C}=O \longrightarrow R\cdot + CO \qquad (2)$$

$$R\cdot + RCH=O \longrightarrow RH + R\dot{C}=O \qquad (3)$$

$$R\cdot + R'SH \longrightarrow RH + R'S\cdot \qquad (6)$$

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[1] We are pleased to acknowledge support of this work by the U.S. Atomic Energy Commission, AT(30-1)2499.

[2] S. Winstein and F.H. Seubold, J. Amer. Chem. Soc. 69, 2917 (1947).

[3] D.Y. Curtin and M.J. Hurwitz, J. Amer. Chem. Soc. 74, 5381 (1952).

[4] J.B. Conant, C.N. Webb and W.C. Mendum, J. Amer. Chem. Soc. 51, 1246 (1929).

[5] G.K. Rollefson and D.C. Grahame, J. Chem. Phys. 7, 775 (1939).

[6] E.F.P. Harris and W.A. Waters, Nature, Lond. 170, 212 (1952).

The mercaptan may react very readily with the initiator-derived radical I• (reaction 4), and/or the aldehyde-derived radical R•(reaction 6). It is converted to the thiyl radical RS•, which is a more effective abstractor of hydrogen than is the hydrocarbon radical R,[6,7,8] leading to more effective chain initiation (reaction 5), and possibly to more effective chain propagation also (reactions 6, 5 and 2). Photolysis of disulfides also leads to the thiyl radicals,[8,9,10] and it seemed of interest to examine the light-induced decarbonylation in the presence of disulfides and mercaptans.

Reactions were carried out in a Pyrex 3-neck flask equipped with magnetic stirrer, thermometer, heating bath, Dean-Stark trap, gas-inlet tube, dropping funnel and a gas buret for measuring evolved carbon monoxide. Irradiation was by a 275 watt RS sunlamp set 6 cm from the reaction flask. 2-Ethylhexanal, with or without additive, was placed in the flask; the system was evacuated for about 15 min and then swept with helium or oxygen-free nitrogen for one hour; the flask was brought to 140-145°, irradiation was begun and the rate of evolution of carbon monoxide was measured, maximum rate (R_{max}) being noted. The results of some of the experiments are summarized in Table 1.

In the absence of additive, decarbonylation occurred slowly with a maximum rate of about 0.03% per min, and 9% yield of heptane after 20 hr. Three disulfides were examined in 3-4 mole percent concentration, leading to a five- to ten-fold increase in maximum rate of decarbonylation. Thioglycolic acid disulfide (TGAD) seemed to lose its effectiveness in a few hours and a low yield of hydrocarbon was obtained. Diphenyldisulfide

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[7] A.F. Bickel and E.C. Kooyman, Nature, Lond. 170, 211 (1952).

[8] C.H. Wang and S.G. Cohen, J. Amer. Chem. Soc. 79, 1924 (1957).

[9] M.S. Kharasch, W. Nudenberg and T.H. Meltzer, J. Org. Chem. 18, 1233 (1953).

[10] Y. Schaafsma, A.F. Bickel and E.C. Kooyman, Tetrahedron 10, 76 (1960).

was more effective. Dibenzyldisulfide led to a more rapid rate and was effective over a long period, leading after 20 hr to 68% yield of heptane and 17% recovery of starting material. This decarbonylation started slowly, rose to its maximum rate after 2-3 hr and gradually tapered off. It appeared that an effective initiator or propagator was being formed during the reaction, probably the mercaptan, which is required in any event for

TABLE 1

Light Induced Decarbonylation of 2-Ethylhexanal

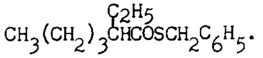
Exp. no.	Aldehyde mole	Additive		Time[b] hr	$R_{max}(CO)$ mmole per min	Heptane % yield	Aldehyde % rec'd.
		Compound	mmoles				
1	0.20	-	-	20	0.06	9	40
2	0.13	TGAD[a]	5.0	5	0.28	12	-
3	0.16	$\phi SS\phi$	5.0	6	0.30	32	27
4	0.13	$\phi CH_2SSCH_2\phi$	5.0	20	0.60	68	17
5	0.16	$\phi CH_2SSCH_2\phi$	5.0	0.3	0.14	-	-
	0.03	ϕCH_2SH	2.5	7.2	1.4	55	14
6	0.16	ϕCH_2SH	5.0	5.0	3.0	39	39

[a] Thioglycolic acid disulfide.
[b] Total irradiation time.

the proposed reaction 6 in the chain sequence. An experiment was then carried out (exp. 5) in which some benzyl mercaptan was added while the disulfide catalyzed reaction was in its early slow stage. A rapid increase of rate, to about 0.7% per min, resulted and a 55% yield of heptane was isolated after 7.5 hr. When benzyl mercaptan was present initially (exp. 6), without added disulfide, the maximum rate of decarbonylation was reached in a few minutes and was very high, 1.9% per min, some fiftyfold greater than the uncatalyzed rate, and corresponding in this experiment to evolution of about 75 cc of carbon monoxide per min. However, the rapid reaction slowed down markedly, essentially stopping after a few hours; the yield of heptane, 39%, was satisfactory in view of the high recovery of the aldehyde. Furthermore, in another run, addition of more mercaptan after the reaction had slowed down led to renewed rapid decarbonylation, indicating that the decrease in rate was due not to loss in capacity to absorb the light, but to the rapid reaction being accompanied by rapid termination processes involving thiyl radicals, which consumed mercaptan.

The termination reaction appeared to be largely combination of the 2-heptyl and benzylthiyl radicals.

$$R\cdot + R'S\cdot \longrightarrow R\text{-}S\text{-}R' \qquad (7)$$

After removal of the undecomposed aldehyde, a higher boiling sulfur containing fraction was obtained, the infra-red spectrum of which showed no carbonyl absorption but was in many other respects similar to that of a synthesized sample of benzyl 2-ethylthiohexanoate  $CH_3(CH_2)_3\overset{C_2H_5}{\overset{|}{C}}HCOSCH_2C_6H_5$. The latter did not appear to be formed, the 2-ethylhexanoyl radical apparently losing carbon monoxide rapidly[11] under the conditions of atmospheric pressure and rather high temperature of these experiments (reaction 2). Also, little disulfide seemed to be formed from the mercaptan. Contrary to our expectations, photolysis of disulfide may be relatively unimportant in the initiation of decarbonylation.

Mercaptan may accelerate the decarbonylation by leading to a more rapid chain propagating sequence, reactions (6) and (5), as noted above. However, it is not clear what the initiation step is in the light-induced reaction, and mercaptan may well be effective also by reacting with excited aldehyde

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[11] R. Cramer, J. Amer. Chem. Soc. 79, 6215 (1957).

(reaction 8),

$$RCH = \overset{*}{O} + R'SH \longrightarrow RCHOH + RS\cdot \qquad (8)$$

leading to more efficient use of the absorbed light and formation of the reactive thiyl radical. Similarly, formation of thiyl radicals from direct reaction of initiator-derived alkyl radicals with mercaptan in the dimethyl 2,2'-azo-isobutyrate initiated decarbonylation (reaction 4) may be important in leading to more effective utilization of that initiator.[6] The ability of mercaptans to react with unreactive initiator-derived radicals before they may dimerize, increasing overall reactivity, has been described in the case of diphenylmethyl radical.[8]

It is of particular interest that in these experiments mercaptan leads to accelerated reactions subsequent to photoexcitation of an aldehyde. In other work, mercaptans have led, on the contrary, to retardation and inhibition of the non-chain light-induced reduction of benzophenone to benzopinacol by 2-propanol.[12] Those results were interpreted in terms of repeated hydrogen transfer processes by mercaptan and thiyl radical. On the basis of other evidence, it was proposed that the mercaptans may not act as quenchers for the excited state of the carbonyl compound, a conclusion consistent with the results now being reported.

In this connection some preliminary experiments have been carried out, with the apparatus described above, on the benzophenone sensitized decarbonylation of aldehydes (Table 2). Although the maximum rate is not very high, benzophenone (0.3 m/l., exp. 7) sensitizes the decarbonylation of 2-ethylhexanal, leading to a rate about five times that in its absence (cf. exp. 1). The reaction proceeds at a rather uniform rate, leading to 42% yield of heptane when the reaction was interrupted after 12 hr.

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[12] S.G. Cohen, S. Orman and D. Laufer, Proc. Chem. Soc., 301 (1961).

The benzophenone was recovered in high (85%) yield, and higher conversions would undoubtedly result from longer irradiation. This reaction was unaffected by the presence of 2-mercaptomesitylene (exp. 8), a mercaptan which was but little effective when used alone in decarbonylation of 2-ethylhexanal, but had been very effective in inhibiting the reduction of benzophenone.[12] This provides confirmation that the inhibitory effect in the latter case did not arise from desensitizing or quenching. Addition of the effective catalyst, benzyl mercaptan (exp. 9) led to rapid decarbonylation, apparently at a rate greater than would be expected from the sum of those due individually to the benzophenone and this quantity of mercaptan. This is consistent with more rapid initiation due to the benzophenone and more rapid propagation due to the mercaptan. It does not exclude the mercaptan's leading to more rapid initiation. Finally, it may

TABLE 2

Light-induced Decarbonylation of Aldehydes

Exp. no.	Aldehyde		Additive		R_{max}(CO)
	Compound	mole	Compound	mmoles	mmole/min
7	2-Ethylhexanal	0.20	$\phi_2C = O$	10	0.3
8	2-Ethylhexanal	0.20	$\phi_2C = O$ MesSH[a]	10 2	0.3
9	2-Ethylhexanal	0.20	$\phi_2C = O$ ϕCH_2SH	10 2	3.4
10	Heptanal	0.20	$\phi_2C = O$	10	0.3
11	Heptanal	0.20	ϕCH_2SH	10	0.2
12	Hydrocinnamaldehyde	0.30	$\phi_2C = O$	15	0.3

[a] 2-Mercaptomesitylene.

be noted that benzyl mercaptan is most effective in decarbonylation of the α-branched 2-ethylhexanal and far less effective with the unbranched aldehyde (exp. 11), whereas benzophenone has a similar sensitizing effect on 2-ethylhexanal, n-heptaldehyde and hydrocinnamaldehyde (exp. 7, 10 and 12).