## PHOTOOXIDATION OF KETONES IN AN O<sup>18</sup> ENRICHED ENVIRONMENT<sup>1</sup>

J. R. DUNN<sup>2</sup> AND K. O. KUTSCHKE

## ABSTRACT

A technique is described in which the origins of the products of photooxidation of ketones can be obtained in respect to whether they arise from the carbonyl or the alkyl groups of the ketone molecule. This is accomplished with the use of reactant molecular oxygen which has been enriched in the O<sup>18</sup> isotope. Application of this to the photooxidation of acetone indicates that a large fraction of the carbon dioxide contains the carbonyl group of the ketone and that acetyl radicals play an important role in the oxidation to temperatures at least as high as 175° C. Propionyl radicals are much less stable, and, in the photooxidation of diethyl ketone, their reactions, other than decomposition, appear to be negligible at quite low temperatures. Some comment is made on the mechanisms of these photooxidations.

In the course of recent work on the photooxidation of azomethane it was observed that relatively small amounts of the oxides of carbon were produced (1). In particular, it has been suggested (1) that, under the conditions used in these experiments, methyl radicals are not oxidized to carbon dioxide to any large extent and that the greater amounts of the dioxide found in the photooxidation of acetone (2) must have arisen from an oxidation of the carbonyl group. Such an oxidation might occur, for example, by reactions of acetyl radicals (3) or acetonyl radicals (1) with oxygen. This disagrees with the work of Christie (4), who observed that essentially all of the carbon dioxide was radioactive when produced in the photooxidation of  $C^{14}H_3COC^{14}H_3$ . In view of this contradiction and of the impure acetone sample used by Christie (some unidentified material which led to unexpectedly large yields of carbon dioxide (4)), it was thought worth while to check the result by an independent method.

If oxygen enriched in  $O^{18}$  is used in these experiments, any carbon dioxide containing the methyl carbon atom will show the same  $O^{18}$  enrichment as does the reactant oxygen. Conversely, if the carbonyl group is the source of the dioxide and if it is assumed that the carbonyl group survives the reaction without rupture of the C—O carbonyl linkage, the carbon dioxide produced will show only one-half the enrichment of the reactant oxygen. By a similar argument, carbon monoxide which arises from the carbonyl group, for example by the decomposition of acetyl radicals, will possess the natural isotopic composition, while that which is formed from the terminal carbon atom will be enriched to the same extent as is the reactant oxygen. Similar considerations show that formaldehyde that arises from the carbonyl group will have the natural abundance of  $O^{18}$ , while that arising from methyl radical oxidation will be enriched.

The carbon monoxide observations also aid in the investigation of the primary products of ketone photolysis. It seems well established that methyl and acetyl radicals are the first radicals produced from the excited acetone molecule formed by light absorption at  $\sim$ 3130 Å (5). Acetyl radicals so formed are energy rich, and a certain fraction of them are thought to decompose before experiencing any significant number of collisions. The remainder react as acetyl radicals, the predominant reaction being decomposition into carbon monoxide and a methyl radical presumably by a quasi-unimolecular process (6), so that

Can. J. Chem. Vol. 36 (1958)

Can. J. Chem. Downloaded from www.nrcresearchpress.com by University of Queensland on 07/18/13. For personal use only.

<sup>&</sup>lt;sup>1</sup>Manuscript received October 29, 1957.

Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada.

Issued as N.R.C. No. 4599. <sup>2</sup>National Research Council Postdoctorate Fellow 1953–55. Present address: British Rubber Research Association, Welwyn Garden City, Herts., England.

 $\Phi_{co}$  is temperature dependent. General confirmation of this is found in the observations made here, which indicate that the extent of decomposition of the acetyl radical varies with temperature at a given oxygen pressure.

An analogous argument may be made in the case of diethyl ketone photooxidation in which the primary process is thought to differ only in degree from that in acetone (7). Substantiation for such a view may be deduced from the data presented here.

Only preliminary results appear here; more detailed investigations are reported in forthcoming publications from these laboratories. Since this work was completed, the results of Taylor and Blacet (8) appeared; these authors presented a similar treatment of biacetyl photooxidation.

### EXPERIMENTAL

Experimental procedures were similar to those used previously in these laboratories (1) with a few exceptions. The reaction cell together with a magnetically driven stirrer was housed in a thermostatted air oven. A few centimeters of 8 mm. tubing were external to the oven and connected via glass float-valves to a mercury cutoff, leading to the storage and analytical systems, and to a small Toepler pump which served to "dose" oxygen into the reaction system as required to maintain the oxygen pressure constant to within some 10-15%. The system appeared to prevent the polymerization of formaldehyde during exposure since reproducible recoveries from the LeRoy still (9) were achieved for this product. The carbon monoxide – oxygen fraction, removed at  $-196^{\circ}$  C., was slowly introduced into a vessel containing a fresh surface of yellow phosphorus. With sufficiently slow introduction negligible oxidation occurred; blank experiments showed no exchange during this procedure. Carbon monoxide recovered was submitted for mass spectrometric analysis. The carbon dioxide fraction, separated at  $-160^{\circ}$  C., was submitted for mass analysis with no further treatment; small amounts of formaldehyde were always present. The bulk of the formaldehyde was recovered with prolonged pumping at  $-130^{\circ}$  C. and submitted for isotopic analysis. Higher-boiling compounds were not investigated in the work reported here.

Analogous procedures were used with diethyl ketone; formaldehyde was absent but acetaldehyde was a major product. Some  $C_2$  hydrocarbon was also found.

Acetone and diethyl ketone were good quality commercial products, carefully dried and outgassed. Oxygen was obtained from the slow electrolysis, *in vacuo*, of about 1 cm.<sup>3</sup> of outgassed, enriched water (from Dr. L. C. Leitch of these laboratories) using a drop of sulphuric acid as an electrolyte. The oxygen was led over platinized asbestos at 300° C., and then through several liquid nitrogen traps to storage. Mass spectrometric analysis yielded a 34/32 ratio  $2.90 \times 10^{-2}$  (natural  $0.34 \times 10^{-2}$ ) indicating that 2.8% of the oxygen molecules contained an atom of O<sup>18</sup>. The same procedure was followed with water stated to contain 10.17% O<sup>18</sup> (Dajac Laboratories); analysis of the oxygen gave 9.59 atom %O<sup>18</sup>. Only a few experiments, not reported here, were made with the more highly enriched oxygen; they were in essential agreement with the results reported.

#### RESULTS AND DISCUSSION

With conditions of acetone and oxygen pressures, absorbed light intensity, and temperature similar to those used by earlier workers (2, 4, 10), over-all quantum yields for the production of the oxides of carbon and for the consumption of oxygen were in excellent agreement. However, the fraction of the total carbon monoxide produced which contains the carbonyl group,  $x_1$ , varies with temperature and oxygen pressure as shown in Table I.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by University of Queensland on 07/18/13 For personal use only.

# DUNN AND KUTSCHKE: PHOTOOXIDATION OF KETONES

	O2 (mm.)	$x_1$	$x_2$	$x_3$
Acetonea				
120° C.	0.08	0.25	0.92	
	0.17	0.22	0.92	
	0.3	0.18	0.94	
	0.5	0.0	0.83	
175° C.	0.08	0.73	0.88	
	0.56	0.12	0.82	
	0.99	0.43	0.80	
	2.0	0.12	0 80	
	14		0.81	
Diethyl ketone <sup>b</sup>				
120° C.	0.33	0.87	0.79	0.52
	0.84		0.79	
	16	0.90	0.90	0.56
175° C.	0 4	0.88	0.74	0.32
	$\tilde{0}$ $\tilde{7}$	0.89	0 69	0 29
	1.3	0.77	0.55	0.29

TABLE I									
Origin of	THE	OXIDES C	)F	CARBON	IN	KETONE	рнотос	XIDATI	ION

<sup>a</sup>Ketone pressure 13 cm.;  $I_a \sim 2 \times 10^{12}$  quanta cm.<sup>-3</sup> second<sup>-1</sup>;  $\lambda \sim 3130$  Å;  $\sim 0.5\%$  decomposition.

<sup>b</sup>Kelone pressure 3.5 cm.;  $I_a \sim 1 \times 10^{12}$  quanta cm.<sup>-3</sup> second<sup>-1</sup>;  $\lambda \sim 3130$  Å;  $\sim 1\%$  decomposition.

The trend, aside from one experiment at  $175^{\circ}$  C., indicates that even at these temperatures acetyl radical lifetime is sufficiently long to allow a reaction with oxygen which apparently does not produce carbon monoxide. This is in agreement with the observations of McDowell and Thomas (11), who observed that acetyl radicals reacted with oxygen, rather than decomposed, as high as 200° C.

Only a small fraction  $(1-x_2)$  of the carbon dioxide ever arises from the methyl group (Table I). It is felt that this conclusion is more reliable than that reached by Christie (4) in view of the uncertainty, mentioned earlier, in the latter work. Moreover, it agrees with the observation that, in the absence of carbonyl groups in the substrate molecule, carbon dioxide is a minor product of methyl radical oxidation (1).

Attempts were made to determine the origin of the formaldehyde product by observing the 32/30 ratio in its mass spectrum. The results were inconclusive, however, since the 32 residual varied in an unpredictable manner whenever formaldehyde was present in the sample chamber.

Some experiments were done on the diethyl ketone photooxidation; the data are included in Table I. Absolute values of quantum yields were again in essential agreement with those of other workers (12, 13). Two experiments at room temperature yielded negligible amounts of carbon monoxide (other workers found  $\Phi_{CO} \sim 0.1$  for similar conditions); the carbon dioxide from the room temperature experiments all contained the carbonyl group. The higher values for  $x_1$  from diethyl ketone as compared to those from acetone at the same temperature and oxygen pressure presumably reflect the greater ease with which propionyl radicals decompose. Carbon dioxide could arise in part by mechanisms analogous to those suggested earlier for acetone, but at the higher temperatures a mechanism must exist which produces carbon dioxide from the ethyl group of the ketone. This conclusion is in harmony with the carbon-14 tracer data obtained by Finkelstein and Noyes (12). It is to be noted that the mechanism proposed by Jolley (13) does not take this fact into consideration. The origin of the acetaldehyde found here ( $x_3$  is that fraction of the aldehyde which contains the carbonyl group of the ketone—see Table I) cannot be explained simply. The present result disagrees with the conclusion of Finkelstein and Noyes (12), who found that essentially all the acetaldehyde arose from ethyl radical oxidation. No explanation can be offered for this disagreement. The possibility of exchange between acetaldehyde and reactant oxygen (mostly O<sup>16</sup>) cannot be ruled out on the basis of present data.\*

Much more data are obviously required before a consistent mechanism can be written for either of these photooxidations; tracer experiments are of particular importance. It is felt that the technique outlined here presents a means whereby such data may be obtained relatively simply since the enriched oxygen is readily prepared.

## ACKNOWLEDGMENTS

The authors wish to thank Dr. E. W. R. Steacie for the interest expressed throughout this work, and Mrs. June Garlick and Mrs. Frances Kutschke for the mass spectrometric analyses.

## REFERENCES

- 1. HOEY, G. R. and KUTSCHKE, K. O. Can. J. Chem. 33, 496 (1955).
- 2. MARCOTTE, F. B. and Noves, W. A., Jr. J. Am. Chem. Soc. 74, 783 (1952); Discussions Faraday Soc. 10, 236 (1951).

  - HENTZ, R. R. J. Am. Chem. Soc. 75, 5810 (1953).
    CHRISTIE, M. I. J. Am. Chem. Soc. 76, 1979 (1954).
    NOYES, W. A., Jr. J. Phys. & Colloid Chem. 55, 925 (1951).
    HOARE, D. E. Trans. Faraday Soc. 53, 791 (1957).
    STEACIE, E. W. R. Atomic and free radical reactions. Reinhold Publishing Corporation, New York. 1954.
- 1304.
  TAYLOR, R. P. and BLACET, F. E. Ind. Eng. Chem. 48, 1505 (1956).
  LEROY, D. J. Can. J. Research, B, 28, 492 (1950).
  HOARE, D. E. Trans. Faraday Soc. 49, 1292 (1953).
  MCDOWELL, C. A. and THOMAS, J. H. J. Chem. Soc. 2208, 2217 (1949); Discussions Faraday Soc. 10, 200 (1071). 310 (1951).
- 12. FINKELSTEIN, A. and NOYES, W. A., Jr. Discussions Faraday Soc. 14, 76 (1953). 13. JOLLEY, J. E. J. Am. Chem. Soc. 79, 1537 (1957).

\*We are indebted to the referee for drawing our attention to this point.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by University of Queensland on 07/18/13 For personal use only.