spectra indicated the formation of about 2 × 10^{-5} mole of N_2O in the combustion gases from experiments with large amounts of sulfur and 5 atm. of air. Nitrous oxide presumably formed when higher oxides of nitrogen were reduced in the oxidation of SO_2 to aqueous sulfuric acid. As indicated in Table II, a correction for formation of N_2O, based on the value of the heat of formation from ref. 2, was applied to the results for $C/S = 2$.

The amount of N_2O in the final state probably depends on reactions on the surface of the hot crucible. In experiments in which a fused-silica crucible instead of a platinum crucible was used, significant amounts of N_2O sometimes were formed, and the evolution of energy was lower than when platinum crucibles were used. The results obtained with fused-silica crucibles were rejected and are not reported here.

The effect of differences in purity of sulfur samples also could explain the difference between the values of the present investigation and those listed in ref. 8.

Comparison with Previous Work.—The result of this investigation for the heat of formation of $H_2SO_4 \cdot 115H_2O$ is compared with other values in Table III. If experiments in progress at the University of Lund confirm the preliminary value quoted in Table III, this important thermochemical datum will have been defined independently in two laboratories within ±0.1 kcal. $mole^{-1}$, or better.

TABLE III

COMPARISON WITH PREVIOUS WORK

Source	Sulfur sample	$\Delta Hf^\circ_{298.16}$ ($H_2SO_4 \cdot 115\ H_2O$) kcal. $mole^{-1}$
NBS circular 500(1952)[a]		−211.63
USBM (1956)[b]	USBM P1[c]	−212.02
Lund (1956)[b]	SS[d]	−212.39
USBM (1959)[e]	USBM P1b[g]	−212.17
Lund (1959–1960)[f]	USBM P1b[g]	−212.24

[a] Value interpolated from table in ref. 2. [b] Values calculated from results listed in ref. 8, p. 171. [c] Sample described in ref. 7. [d] Sample prepared by S. Sunner, University of Lund. [e] This investigation. [f] Communicated by S. Sunner. This value is from preliminary results of experiments still in progress. [g] Sample described in this paper.

Effect on Values of the Heat of Formation of Organic Sulfur Compounds.—All heat of formation values previously reported by the Bureau of Mines were revised and placed on a more consistent basis by using the newly determined value for the heat of formation of $H_2SO_4 \cdot 115\ H_2O$. Most of the originally published values were changed by an amount less than the experimental uncertainty. The revised values will be given in comprehensive tabulations, now in preparation, of the thermodynamic properties of organic sulfur compounds.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF ROCHESTER, ROCHESTER, NEW YORK]

Photochemical Production of Acetone-O^{18} in the System Acetone:$O^{18}{}_2$ at 3130 Å.[1]

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Acetone-O^{18} was observed to be formed on exposure of a mixture of acetone vapor and $oxygen^{18}$ gas to light of 3130 Å. At the same time, no change in the isotopic composition of the oxygen was detected. Oxygen consumption and photo-oxidation of the ketone accompanied the labelling process. The rate of formation of acetone-O^{18}, when corrected for the dark reaction, was found to be independent of oxygen pressure (from 1 to 40 mm.) and temperature (up to 65°) at constant intensity. The quantum yield for the formation of acetone-O^{18}, which was 0.45, was unaffected by a ten-fold change in intensity. The quantum yield for the production of 3-pentanone-O^{18} in the system 3-pentanone:$O_2{}^{18}$ was 0.7. In the photolysis of a mixture of 3-pentanone, azoethane and $O^{18}{}_2$ by light which was absorbed only by azoethane, the formation of 3-pentanone-O^{18} was not observed. It is believed that the photochemical production of the labelled ketones may be a part of the photo-oxidation mechanism.

Introduction

It is known[2] that the phosphorescence of acetone vapor, which presumably arises from a triplet state, is quenched by oxygen. Some features of the quenching suggest that an exchange of an oxygen atom between the ketone and the oxygen molecule may accompany this process. The present study was undertaken to test the idea.

The photo-oxidation of acetone in an O^{18} enriched environment has been studied by Dunn and Kutschke,[3] but an isotopic analysis of the ketone or the oxygen at the end of the photolysis was not reported.

Experimental

Acetone (Eastman Kodak "Spectrograde") was dried over "Drierite" and distilled *in vacuo* before use. $Oxygen^{18}$ (> 98% purity) obtained from the Weizmann Institute of Science, Israel, was used as such.

A conventional high vacuum system was used. In order to conserve materials, the volume of the cell and dead space were kept as small as possible. The quartz cell of 5.0 cm. dia. and 4.4 cm. length (82.5 ml.) was attached to a Toepler pump of about 300 ml. capacity. After the desired quantity of acetone and oxygen had been admitted to the cell, the mixture was stirred by repeated expansion into the large volume. About 60 such cycles were found to mix the reactants thoroughly. During a run the light beam was interrupted at regular intervals and the contents of the cell were stirred. A timer which operated a series of microswitches carried out these operations automatically and recorded the durations of the irradiation and stirring. It was observed that at low oxygen pressures, even at low intensities, the yield of acetone-O^{18} was lower in the absence of mechanical stirring, which suggested that diffusive mixing was not rapid enough to avoid local depletion of oxygen.

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(1) The authors wish to thank the National Science Foundation for a grant in support of this work.

(2) G. W. Luckey and W. A. Noyes, Jr., *J. Chem. Phys.*, **19**, 227 (1951); J. Heicklen, THIS JOURNAL, **81**, 3863 (1959).

(3) J. R. Dunn and K. O. Kutschke, *Can. J. Chem.*, **36**, 421 (1958).

The light source was a Hanovia S-100 medium pressure mercury arc for the experiments at low intensity and a General Electric AH-6 high pressure mercury arc for the ones at high intensity. In both cases, a Pyrex filter was used. The formation of carbon monoxide from pure acetone at room temperature ($\Phi = 0.1$) was used as the actinometer. Since the high pressure arc decayed steadily in intensity, it had to be calibrated at the beginning and end of each run.

Photolysis gave rise to a product that distilled along with acetone at −78° and which was not separable from acetone on a vapor phase chromatograph. In a mass spectrometer this product (when introduced along with acetone) showed a parent peak at mass number 60 and an intense peak at mass 45. It was inferred that this product was $CH_3CO^{18}CH_3$ and that the peak at mass 45 was due to CH_3CO^{18}.

In quantitative studies the fraction volatile at −195° was separated from the fraction volatile at −78° and the mass spectrum of each of these determined on a Consolidated Engineering Co. type 21–620 mass spectrometer. The former consisted of oxygen with traces of carbon monoxide. The latter was mainly acetone with small amounts of water, carbon dioxide (chiefly $CO^{16}O^{18}$) and formaldehyde, which did not interfere with the estimation of acetone-O^{18}. No methane, ethane or biacetyl was detected. The conversion of the ketone was less than 3% with a third of this amount lost by oxidation. The depletion of oxygen ranged from 5% at 16 mm. to about 40% at the lowest pressure used.

Results

On mixing acetone vapor and oxygen^{18} in the dark, acetone-O^{18} was observed to be formed slowly. The reaction proceeded at the same rate at 5 and 15 mm. of oxygen, at constant ketone pressure. An increase in the temperature from 27 to 65°, or vigorous stirring of the mixture caused an increase in the rate. The dark reaction was not accompanied by a change in the isotopic composition of the oxygen.

Irradiation of a mixture of acetone vapor and oxygen^{18} led to the formation of acetone-O^{18} at a rate considerably greater than that of the dark reaction. At the same time no change in the isotopic composition of the oxygen was detected if there was no O_2^{16} present. For example, in a run in which a mixture of 20.1 mm. of acetone and 3 mm. of O^{18}_2 was irradiated, 2.4% of the acetone was converted to acetone-O^{18}. The composition of the oxygen before irradiation was O^{18}_2, 97.83; $O^{17}O^{18}$, 0.386; $O^{16}O^{18}$, 1.729; O^{16}_2, 0.055; (this analysis suggests that exchange equilibrium had not been reached) and after irradiation: O^{18}_2, 97.79; $O^{17}O^{18}$, 0.437; $O^{16}O^{18}$, 1.746; O^{16}_2, 0.057. The change in composition was no more than the uncertainty in the analysis.

When a sample of oxygen which contained 3% of O^{16}_2 was used, it was found that (i) even in the dark on mixing with acetone vapor the fractions of O^{18}_2 and O^{16}_2 decreased while $O^{18}O^{16}$ increased; (ii) on irradiating the mixture the same scrambling as in (i) was observed to take place at a more rapid rate. The rates of the two processes were in the ratio of 1:4. The stoichiometry of the process fitted the equation

$$O^{18}_2 + O^{16}_2 = 2\,O^{18}O^{16} \qquad (1)$$

The rates of formation of acetone-O^{18} under various conditions are listed in Table I. The absolute values of these yields may be uncertain by as much as 10%. This is due to (i) the large correction for the dark reaction which amounted to 25% of the photochemical reaction at the lowest intensity used, and (ii) the inherent difficulty in the estimation of a small quantity of acetone-O^{18} in a large quantity of unreacted acetone. The relative rates may be reliable to ±5% and were found to be reproducible to within this uncertainty.

Table I

Rate of Production of $CH_3CO^{18}CH_3$ at 3130 Å.

Acetone pressure 20 ± 1 mm.; room temperature except when stated otherwise

Oxygen press.,[a] mm.	Time, sec.	Relative intensity	Labelling rate,[c] µm/sec. × 10⁶	Remarks
17.4[b]	63240	1.00	4.65	
16.7	60480	0.98	4.38	Not stirred after initial mixing
17.0[b]	59040	0	1.38	Dark run
16.0[b]	43200	1.00	(5.76)	
18.2[b]	16200	1.00	4.27	0.6% conversion
2.5[b]	61500	1.00	4.60	
1.0[b]	63600	1.00	4.18	
16.7[d]	6600	9.75	45.6	
16.4[d]	6600	8.41	40.7	
41.7[d]	6600	6.00	28.6	
0.7[d]	3600	8.50	15.3	
20.2[d]	6600	4.67	22.0	$T = 65°$

[a] Not corrected for any nitrogen present. [b] Stirred for 5 min. in every hour. [c] Corrected for dark run where necessary. [d] Stirred for 5 min. in every quarter hour.

The quantum yield for the formation of acetone-O^{18} was 0.45. This value was not affected by oxygen pressure, temperature (up to 65°), or a ten-fold change in intensity. The result of one experiment at high intensity and at low oxygen pressure indicated a lower value but the possibility that the stirring was not vigorous enough to keep the reactants well mixed is not ruled out.

A few runs were carried out on the system 3-pentanone:O^{18}_2. The quantum yield for the formation of 3-pentanone-O^{18} was found to be 0.7 at an oxygen pressure of 16 mm. and a ketone pressure of 20 mm. at room temperature. As in the case of acetone, no change in the isotopic composition of the oxygen was detected at the end of the irradiation. In one experiment a mixture of 3-pentanone (20 mm.), azoethane (30 mm.) and O^{18}_2 (18 mm.) was exposed to light filtered by 4 mm. of Corning 3850 glass. Nitrogen was observed to be formed. The isotopic compositions of the oxygen and 3-pentanone showed no detectable change after 2 hr. of irradiation. A blank experiment with azoethane (30 mm.) alone showed that at this pressure and wave length 2.5 µm. of nitrogen was produced in 2 hours.

Discussion

It is most likely that the thermal production of acetone-O^{18} takes place at the wall, which would explain the lack of any effect due to a three-fold change in the oxygen pressure and the dependence of this process on the thoroughness in stirring. The exchanging species at the wall may be H_2O^{18} which was a product of the photochemical oxidation of acetone. Since the thermal reaction was studied after a few photochemical experiments, sufficient H_2O^{18} may have been adsorbed on the walls on the cell. Cohn and Urey(4) have reported that the exchange reaction between acetone and H_2O^{18} in the liquid phase is measurable at 100° but undetectable

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(4) M. Cohn and H. C. Urey, This Journal, **60**, 679 (1938).

at 25°. In the present study, as a wall reaction the exchange may have proceeded at the observed slow rate even at room temperature. This explanation would take into account the lack of any change in the isotopic composition of the oxygen in the thermal reaction.

Since oxygen in a homogeneous gaseous system is an extremely effective scavenger of free radicals, it is unlikely that the photochemical formation of acetone-O^{18} is through a synthesis from radical fragments, *e.g.*, CH_3 and CH_3CO^{18}. Acetone-O^{18} must be formed by an exchange process between an acetone molecule and an oxygen^{18} bearing molecule or radical. The present study does not allow one to decide unequivocally on the nature of the reactants in this reaction. Three possibilities may be considered. In the order of increasing likelihood, these are

(i) $$CH_3COCH_3^* + H_2O^{18} \longrightarrow CH_3CO^{18}CH_3 + H_2O \quad (2)$$

The asterisk denotes a photochemically excited molecule. This reaction is akin to the thermal exchange process but may proceed more rapidly under the same conditions due to the photoenergy available.[5] But since H_2O^{18} is built up in the system only as the photo-oxidation proceeds, (2) will have to compete unfavorably with either the deactivation of the excited ketone molecule by oxygen, or its reaction with oxygen. At least for the triplet state, this is believed to be an extremely efficient reaction. At high oxygen pressure no difference may be seen in the rates of formation of acetone-O^{18} between 0.6% and 2.5% conversions. Hence the build-up of H_2O^{18} (or any other product) does not seem to control the reaction.

(ii) The second possibility is a reaction such as

$$CH_3COCH_3 + RO\cdot^{18} \longrightarrow CH_3CO^{18}CH_2 + RO \quad (3)$$

The radical $RO\cdot^{18}$ may be any of the several oxygen containing intermediates in the oxidation of acetone. The most important criterion is that reaction 3 may not be followed by any step in which the radical $RO\cdot$ gives rise to molecular oxygen, as this would lead to a change in the isotopic composition of the molecular oxygen. It is not obvious which radical species would be likely to take part in (3) and also fulfill the condition mentioned above. From the experiment on 3-pentanone:azoethane: $O_2{}^{18}$, it may be concluded that introduction of ethyl radicals into the system by the photolysis of azoethane is not sufficient to lead to the formation of 3-pentanone-O^{18}.

(iii) A third possibility is the reaction

$$CH_3COCH_3^* + O^{18}{}_2 \longrightarrow \text{complex} \quad (4)$$

$$\text{complex} + CH_3COCH_3 \longrightarrow \left\{\begin{matrix} CH_3CO^{18}CH_3 \\ \text{or} \\ CH_3COCH_3 \end{matrix}\right\} + \text{oxidation intermediates} \quad (5)$$

The reverse of (4) is postulated to be slow and not to result in an exchange of oxygen atoms, while (5) may be a rapid reaction. This reaction scheme, although vague, is capable of explaining the observations. It would not predict a dependence on the intensity, or oxygen pressure (for moderate pressures), which are as observed. It would also predict that the photochemical formation of an O^{18}-ketone may be a general reaction for this class of compounds.

This scheme further suggests that there is a relationship between the formation of acetone-O^{18} and the photo-oxidation process. Hence useful information concerning the two processes may be obtained only by a simultaneous quantitative study of the oxidation products along with the labelled ketone.

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[5] It has been observed in this Laboratory that at 3130 Å. a mixture of acetone and D_2O vapor does not give rise to acetone-*d* or acetone-*d*$_2$ photochemically in detectable amounts. This suggests that any photoexchange process would involve only an oxygen atom and not a –OH group.

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Free Radicals by Mass Spectrometry. XX. Ionization Potentials of Cyclopentadienyl and Cycloheptatrienyl Radicals

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The cyclic free radicals, cyclopentadienyl ($C_5H_5\cdot$) and cycloheptatrienyl (tropenyl) ($C_7H_7\cdot$), have been produced by pyrolytic reactions and identified by mass spectrometry. By electron impact the ionization potentials are found to be: cyclopentadienyl 8.69 ± 0.1 and cycloheptatrienyl 6.60 ± 0.1 v. From thermal and appearance potential data tentative values of the heats of formation of cyclo-$C_7H_7^+$ ion and cyclo-$C_7H_7\cdot$ radical are 217 ± 7 and 65 ± 7 kcal./mole, respectively. Estimated bond dissociation energies are $D(C_7H_7–H)$ in cycloheptatriene = 74 ± 7 kcal./mole and $D(C_7H_7–C_7H_7)$ in ditropenyl 35 kcal./mole. The cycloheptatrienyl radical was produced by thermal decomposition of ditropenyl and the cyclopentadienyl radical by thermal decomposition of anisole. A number of rearrangement reactions in the thermal decomposition of cyclopentadienyl and cycloheptatrienyl derivatives at low pressures have been observed.

On the basis of molecular orbital theory Hückel[3] predicted that monocyclic conjugated systems having $4n + 2$ π-electrons would have large delocalization energies. Representatives of this group with $n = 1$ are the cyclopentadienyl anion ($C_5H_5^-$), the neutral benzene molecule, and the cycloheptatrienyl (tropenium, tropylium) cation ($C_7H_7^+$). Experimental evidence for the stability of the first two

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[1] National Research Council of Canada Postdoctorate Fellow, 1957–1959.

[2] Work at University of Washington supported in part by the Office of Ordnance Research, U. S. Army.

[3] E. Hückel, *Z. Physik*, **70**, 204 (1931); *Z. Elektrochem.*, **43**, 752 (1937).