

the dropping funnel and slowly added to the BaH_2 suspension with stirring. The evolution of hydrogen served as a good indicator for the completion of the experiment. The resulting mixture was filtered through a medium porosity funnel and the pyridine distilled away under vacuum.

The resulting salt was dried at $80\text{--}100^\circ$ in the vacuum oven and analyzed as $\text{BaI}_2 \cdot \text{C}_3\text{H}_7\text{N}$ (pyridine determined by difference). The pyridine was removed by heating the compound to $150\text{--}160^\circ$ *in vacuo*; 28.6 g. of anhydrous barium iodide, a yield of 97%, was obtained. It analyzed 100.1% pure by the gravimetric iodide method. Barium iodide can be kept in a stoppered bottle for months during which time it is only slightly discolored.

The quantity of pyridine used can probably be reduced $1/2$ or $1/4$ since BaI_2 is known to be quite soluble in pyridine.

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The Carbon Monoxide Quantum Yield in the Photolysis of Diisopropyl Ketone¹

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The CO quantum yield in the photolysis of diisopropyl ketone has been measured using di-*n*-propyl ketone as an internal actinometer.^{2,3}

Experimental

The ketones (Eastman Kodak Co. White Label) were stored over Drierite for three months, then distilled through a 12-plate column, the middle fraction being retained. Samples were degassed at about -50° before being used.

The light source was an Hanovia S-100 mercury arc. An essentially parallel beam of light was obtained by a quartz lens and two stops. The light just filled a quartz reaction cell 20 cm. long and 2 cm. i.d., and was then focused by a second quartz lens onto an R. C. A. 935 phototube, connected through a shunt to a Leeds and Northrup type 2290 galvanometer. The reaction cell was contained in an aluminum block furnace, the temperature of which was controlled to $\pm 0.5^\circ$ with a photoelectric relay operating on the light beam from a galvanometer, the latter being actuated by a thermocouple near the reaction cell.

The absorption coefficients of both di-*n*- and diisopropyl ketone were measured at 100° , over a pressure range of from 15 to 90 mm., using essentially 3130 Å. light. For this, filters were used consisting of 3 mm. Corning #9863 (Red-purple Corex), 5 cm. of 0.0005 *M* K_2CrO_4 , 5 cm. of 0.178 *M* NiCl_2 and 2 mm. of Pyrex.⁴ The extinction coefficients were 7.5 ± 0.3 and 9.05 ± 0.15 cm.^{-1} moles⁻¹ liter for the normal and isoketones, respectively.

Inclusion of the K_2CrO_4 filter gave light intensities so low that photochemical runs to determine CO yields would have been prohibitively long. The absorption experiments were repeated without the K_2CrO_4 filter, from which it was concluded that the ketones exhibited the same relative absorptions with $\lambda\lambda$ 3130, 3342 Å. as with λ 3130 Å. alone. It was therefore considered that the use of the polychromatic light was justified in subsequent CO yield determinations.

The CO was measured in a gas buret by pumping off at -210° . When other products² were measured, C_2H_4 was pumped off from a Ward-LeRoy⁵ still at -175° , the C_3 fraction at -135° , *n*-hexane and diisopropyl at -95° . The C_3 fraction was further separated into C_3H_8 and C_3H_6 by analysis in a Blacet-Leighton⁶ apparatus, using the hydroxy-mercurial method.⁷ In the diisopropyl ketone photolysis, no C_2 fraction was found, and the fraction pumped off at -210° was found to be entirely CO by combustion in a CuO furnace.

(1) Issued as N.R.C. No. 3519.

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Results

The carbon monoxide data are shown in Table I.

TABLE I
QUANTUM YIELDS

Run ^a	Temp., °C.	Pres- sure, mm.	Absorp- tion, ^b %	R_{CO} $\times 10^{-11}$, molecules cc. ⁻¹ sec. ⁻¹	$\left(\frac{\text{CO}_{\text{iso}}}{\text{CO}_n}\right)^c$	Φ_n	Φ_{iso}
1	50	34.73	41.8	20.30	3.70	0.25 ^d	0.93
2		19.88	24.6	3.25			
3	75	43.20	46.0	24.10	3.45	.29 ^d	1.00
4		52.50	46.0	6.97			
5	100	18.35	24.0	14.23	2.95	.31 ^e	0.92
6		22.38	24.0	4.83			
7	100	18.23	23.9	13.05	3.22	.31	1.00
8		22.23	23.9	4.05			
9	125	48.11	45.0	26.80	3.16	.31	0.98
10		58.06	45.0	8.50			
11	125	19.00	23.6	14.0	3.18	.31	0.99
12		23.00	23.6	4.35			
13	150	50.40	44.7	25.40	3.30	.31	1.03
14		61.47	45.0	7.76			

^a Odd numbered runs are the iso compound, even numbered are the normal. ^b From absorption data for polychromatic light. ^c Calculated after reducing to the same % absorption for both compounds. ^d Calculated from temperature dependence found by Bamford and Norrish³ and value found by Masson² at 113° . ^e Data of Masson.²

The CO quantum yield for the iso compound is thus seen to be essentially unity in the temperature range $50\text{--}150^\circ$. This indicates that the isobutryl radical is unstable at the lowest temperature.

The following are more comprehensive analyses for the photolysis products of the two ketones at 100° , using a d.c. operated General Electric AH-6 arc⁸ and Pyrex filter. This represents about a two hundred-fold increase in light intensity over that available from the S-100 arc. Ketone pressures were 16.0 mm. Rates are expressed in molecules cc.^{-1} $\text{sec.}^{-1} \times 10^{-13}$.

TABLE II

Ketone	R_{CO}	$R_{\text{C}_2\text{H}_4}$	$\Delta R_{\text{C}_3\text{H}_8}$	$R_{\text{C}_3\text{H}_6}$	$R_{\text{C}_3\text{H}_{14}}$
Normal	6.42	6.25	0.42	0.723	5.46
Iso	24.2	..	.78	7.75	27.1

The column $\Delta R_{\text{C}_3\text{H}_8}$ refers to the difference $R_{\text{C}_3\text{H}_8} - R_{\text{C}_3\text{H}_6}$. On the basis of similar free-radical mechanisms for the two ketones, this represents the C_3H_8 formed by abstraction of H from the ketone by the propyl or isopropyl radical. Comparison of the ratios $\text{C}_3\text{H}_6/\text{C}_3\text{H}_{14}$ shows that disproportionation of radicals plays a greater role, compared to recombination, with the iso compound than with the normal. This is in agreement with the results of Blacet and Calvert⁹ for the photolysis of *n*- and isobutyraldehydes.

Of especial interest is the fact that here the absence of a Norrish type II split¹⁰ is accompanied by a CO quantum yield of unity. The absence of such a primary process in this ketone is expected, and is in accordance with the generally accepted idea that a 3-carbon chain adjacent to the carbonyl group is

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necessary for its occurrence.¹¹ The CO yield of unity places diisopropyl ketone in line with acetone¹² and diethyl ketone^{13,14} both of which show $\Phi_{CO} = 1$ under conditions where the acyl radical is unstable.

(11) NOTE ADDED IN PROOF.—Further work supporting this hypothesis has been published recently, A. J. C. Nicholson, *Trans. Faraday Soc.*, **50**, 1067 (1954).

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The anomalous behavior of di-*n*-propyl ketone, where only about half the absorbed quanta can be accounted for, seems therefore to be associated in some manner with the occurrence of the type II mechanism. Vibrational energy may be dissipated in a cyclic structure such as that suggested by Davis and Noyes¹⁵ for methyl *n*-butyl ketone.

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The Stability of Metalloetioporphyrins toward Acids¹

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In the Fe(III), Co(II), Ni(II) and Zn(II) complexes of etioporphyrin II the metal is displaced by concentrated sulfuric acid without decomposition of the porphyrin. The relative rates of metal displacement in sulfuric acid-acetic acid solution and in HCl-acetic acid solution are Co(II) > Ni(II) < Cu(II) << Zn(II). It is suggested that the stability order of these tetradentate "essentially covalent" compounds places the maximum stability in the Ni(II) complex. The kinetic data obtained for Cu(II) displacement were found to fit best the expression rate = $k[\text{copper etioporphyrin II}]^2(h_0)^4$.

The great stability of certain transition metal complexes of "fused-ring" compounds, such as the porphyrins and the phthalocyanines, has long been recognized. This stability is demonstrated by their extreme reluctance to undergo exchange and replacement reactions with radioactive metal ions in solutions³⁻⁵ and by the necessity of using the strongest mineral acids for the displacement of certain metals.^{6,7} Hill⁸ reported that concentrated sulfuric acid was required for the displacement of Mn, Fe(III), Co(III), Ni(II) and Cu(II) from the respective hematoporphyrin complexes. The quantitative nature of the reaction was demonstrated when yields greater than 96% of etioporphyrin II (to be called Etio from now on) were obtained by treating copper etioporphyrin II (to be called CuEtio) with concentrated sulfuric acid.⁹

We have found that the Cu(II), Fe(III), Co(II), Ni(II) and Zn(II) complexes of Etio on treatment with concentrated sulfuric acid give immediately a sharp acid Etio spectrum and no other discernible bands. It was not feasible to obtain measurable rates by carrying out the reactions in an aqueous sulfuric acid medium due to the insolubility of these complexes in even slightly aqueous media. However, for the Ni(II), Cu(II) and Zn(II) complexes it was possible to follow the rates of metal displacement

in sulfuric acid-acetic acid solutions. Acetic acid is an adequate solvent for the metallo Etio complexes and is sufficiently acidic to permit discrimination among very high acidities.^{10,11} However, the Co(II) and Fe(III) complexes underwent considerable decomposition in this medium.

Qualitative experiments showed that in 0.5 *M* sulfuric acid in acetic acid at room temperature, Cu(II) and Zn(II) are removed very rapidly whereas Ni(II) is removed very slowly, if at all. In 1.0 *M* sulfuric acid in acetic acid Ni(II) removal was detected in ten minutes. In solutions less than 0.5 *M* in sulfuric acid Cu(II) is removed much more slowly than Zn(II). In HCl-acetic acid solutions Cu(II) and Co(II) were removed much faster than Ni(II). These qualitative experiments establish the relative rates of displacement in sulfuric acid-acetic acid solution and in HCl-acetic acid solution as Co(II) > Ni(II) < Cu(II) << Zn(II).

In an attempt to replace Zn(II) with another metal ion, ZnEtio was refluxed for several hours in boiling pyridine with NiAc₂, with CuAc₂ and with SnCl₂. In no case was there a detectable replacement of Zn(II) with the metal ion in solution. Barnes and Dorough⁵ found detectable replacement of Zn(II) by Cu(II) in one hour under these conditions with tetraphenylporphyrin complexes, whereas with the Etio complexes we could detect no replacement even after four days. We attribute this difference to the steric interference of the phenyl groups with the porphyrin ring.

The relative rates of the metal ion displacements suggest a stability order with Ni(II) the most stable—Co(II) < Ni(II) > Cu(II) >> Zn(II). Clearly, one is not justified in assuming a strict parallel between rates and equilibria. However, in this instance there is some additional support for this stability order for these square-planar "essentially covalent" complexes. Firstly, in certain iso-

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