

The Pyrogenetic Formation of Ketones

R. I. Reed

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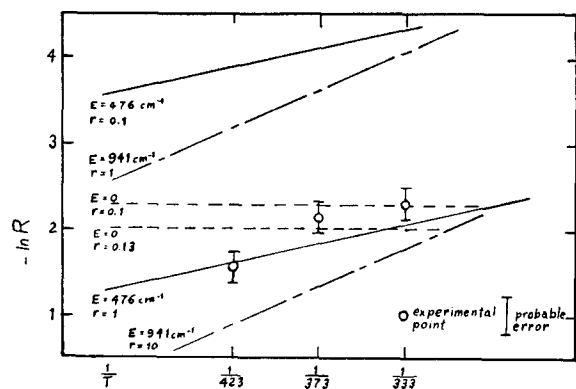


Fig. 1. Measured values of $-\ln R$ compared with theoretical curves of $-\ln R$ versus $1/T$ for possible values of E and r .

existing for the 0-1 band. The same situation is met in heavy naphthalene.

To test the different possibilities, the temperature dependence of the two bands has been investigated. Two methods have been used. First, the number of molecules in the absorption cell was maintained constant, and the two bands were photographed in first order with a 3 m grating spectrograph at 150°C, 100°C, and 60°C. The lower temperature is limited by the vapor pressure necessary to bring out the bands of interest, and the upper limit is determined by the Boltzmann factors. Unfortunately, this makes the useful temperature range very small. From the microphotometer traces of the plates, the quantity $R \approx e^{-E/kT}$ could be measured. r is the transition probability of the 1-0 band relative to that of the 0-1 band, and E is the energy difference between the ground states of the two bands (Fig. 1). Second, the number of molecules in the absorption cell was varied by changing the pressure at a constant temperature of 100°C sufficient to compensate for the Boltzmann factor of an assumed 476 cm^{-1} vibration in the ground state of the 31 513 cm^{-1} band. r appeared to be the order of 1 (Fig. 2).

From the microphotometer traces of several exposures made at different exposure times, the measurements of optical density could be restricted to the region of the plates where it was found to be linear to within 10 percent. Probable errors were calculated on the basis of a 476 cm^{-1} difference between the two ground states neglecting the effect of deviations of naphthalene vapor from a perfect gas and the changing effect of collisions with pressure and temperature.

Examination of Fig. 1 suggests the existence of an energy difference between the ground states of the two bands. This result conforms to the assignment of a forbidden transition for the 3200-2900 Å system. Although these data should not be regarded as an actual measurement of the energy difference, the reasonable value of $r \sim 1$ requires that the difference be of the order of 500 cm^{-1} .

Although the method was somewhat crude and the results meager, they are presented here because it is felt that each additional contribution to the settlement of this assignment problem should be of value. This problem cannot be regarded as completely solved until all of the existing difficulties have been removed.

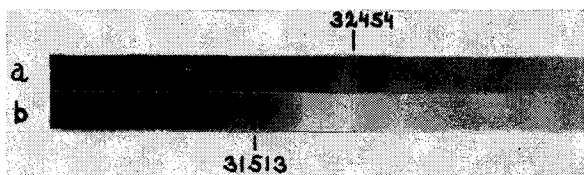


Fig. 2. Photographs from plates taken (a) at 100°C, 1.41 mm Hg, and (b) at 100°C, 8.84 Hg.

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The Pyrogenetic Formation of Ketones

R. I. REED

The University, Glasgow, Scotland
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A MECHANISM, analogous to the "acetoacetic ester" condensation, proposed for the pyrogenetic formation of cyclic ketones,¹ has now been extended to include the formation of ketones from salts of the barium acetate type.² This mechanism is dependent on the presence of an α -hydrogen in the molecule, and thus it is necessary to attribute the formation of benzophenone to a special mechanism.

It is considered that this extension is not supported by the available evidence, and that the thermal decomposition of the alkali and the alkaline earth salts of benzoic, acetic, and isobutyric acids proceed by a mechanism involving free radicals.

The formation of benzaldehyde by the pyrolysis of mixtures of barium benzoate and barium formate at 450°C using an isotopic tracer technique, show that the aldehydic carbon is derived from the formate present.³ The formation of benzene both in this reaction and in benzophenone formation is regarded as evidence of free radical formation, one of the reactions of the phenyl radical being the abstraction of a hydrogen to yield benzene.⁴ The elevated temperatures necessary for significant reaction in this and similar compounds has already been adduced, in the case of acetaldehyde,⁵ as evidence for a radical process.

The decomposition of sodium acetate is being studied in an attempt to determine the kinetic course of the reaction. These experiments are not yet concluded, but a series of measurements carried out in the temperature range 420°-500°C show that the reaction, followed by the formation of sodium carbonate, is of the order 3/2 with respect to the salt for at least 60 percent of the reaction, as shown in Fig. 1.

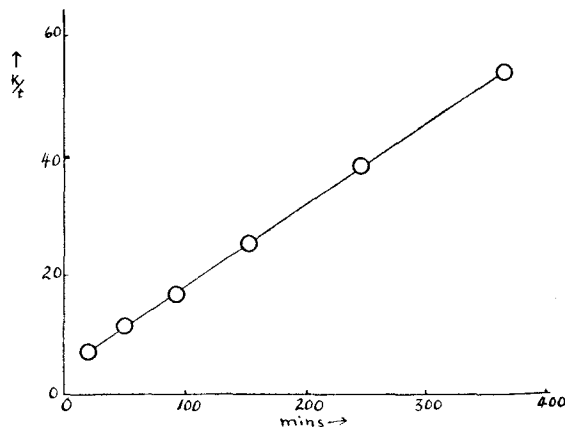


Fig. 1. K/t is plotted for values of the sodium carbonate formed, expressed as a percentage of the total possible reaction.

TABLE I.

Temp. °C	Ketone, as a % of the isobutyrate decomposed			
	Total	Di- <i>n</i> -propyl	Isopropyl- <i>n</i> -propyl	Di-isopropyl
380	100	43.1	43.7	13.2
420	100	44.9	41.9	12.2
460	35	19.0	12.0	3.7
500	13.3	8.8	3.4	1.1
540	8.0	5.7	1.8	0.4

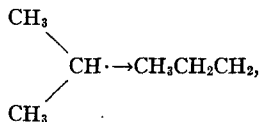
An evaluation of the activation energy indicates that in the above temperature range, the value is nearly 50 kcal mol⁻¹. It is considered that this energy value and the nonintegral reaction order which is most readily interpreted as a chain reaction are consistent with a radical process.

The pyrolytic decomposition of isobutyric acid over a catalyst has been carried out with a careful analysis of all products.⁶ In addition to the anticipated yield of di-isopropylketone, a small quantity of isopropyl-*n*-propylketone was obtained, and this was interpreted as resulting from an abnormal type of "Claisen" condensation. Attention was directed to the numerous other products, all of which could be obtained by the decomposition of the parent ketones. This variety of products has more recently been adduced as evidence for the radical nature of the reaction.⁷

Experiments on the pyrolysis of sodium isobutyrate⁸ have yielded quantities of all three di-propylketones, as shown in Table I.

These experiments were carried out by pyrolyzing about one gram of sodium isobutyrate for a definite period of time at the appropriate temperature. The ketone formed was determined by preparing and weighing a derivative, and the decomposition of the isobutyrate was determined by estimating the sodium carbonate formed. The decomposition of the salt as a percentage of the original amount present, varied from 5-90 percent in these experiments.

These experiments are being continued in an investigation into the nature of the rearrangement. The results so far obtained are most readily interpreted by means of the following radical rearrangement:



which has already been reported in the study of acetaldehyde formation.⁵ A rearrangement of this type is implicit in one mechanism considered by Hamonet⁹ as a means of interpreting the results of the electrolysis of potassium *n*- and *i*-butyric acids, and a similar explanation has been proposed in the photolytic decomposition of di-isopropylketone.¹⁰

These investigations are being continued and extended to include comparative studies on the formation of cyclic ketones.

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Synthesis of Cyclobutene-*d*₆ and Cyclobutane-*d*₈

R. C. LORD

Department of Chemistry, Massachusetts Institute of Technology,
Cambridge, Massachusetts

(Received December 12, 1952)

THE recent paper of Dunitz and Schomaker¹ serves to emphasize the fact that the spectroscopic work on cyclo-

butane reported in the literature some time ago needs to be repeated with the improved infrared equipment now available. This need was also seen in our laboratory, and study of the spectra of the molecule was undertaken. However, it seemed most desirable to study also the deuterium derivative cyclobutane-*d*₈, because of the well-known advantages^{2,3} of isotopic molecules in the analysis of vibrational spectra.

Cope, Haven, Ramp, and Trumbull⁴ have recently described a method of synthesis of cyclobutene that lends itself to the preparation of cyclobutene-*d*₆. In this procedure cyclo-octatetraene is reduced to 1,3,5-cyclo-octatriene, which is in equilibrium with bicyclo [4.2.0] octa-2,4-diene. A Diels-Alder addition of acetylene dicarboxylic methyl ester to the 2- and 5-positions of the bicyclo-octadiene then gives a tricyclic compound which cleaves readily on heating into dimethyl phthalate and cyclobutene. The latter can be hydrogenated easily to cyclobutane.

The changes in the synthesis of Cope *et al.*⁴ to adapt it to the deuterium preparation are straightforward. Cyclo-octatetraene-*d*₈ is prepared by the polymerization of acetylene-*d*₂⁵ and is reduced to cyclo-octatriene-*d*₁₀ by addition of lithium in ether with subsequent decomposition by deuterium oxide. Addition of the dimethyl acetylene dicarboxylate is then carried out as described by Cope *et al.*, as is the thermal decomposition of the adduct. Some 7.0 grams (0.12 mole) of cyclobutene-*d*₆ have been obtained by this procedure.

The cyclobutene-*d*₆ can be handled conveniently by addition of bromine to form the higher-boiling dibromo-cyclobutane, from which it is readily regenerated by treatment with zinc dust in alcohol.⁶ Spectroscopic study of cyclobutene and cyclobutene-*d*₆ is now in progress and, upon completion of this study, that of cyclobutane and cyclobutane-*d*₈ will be carried out. This investigation is part of a general study of the spectra of simple hydrocarbons and their deuterium derivatives supported by the Office of Ordnance Research under Contract DA-19-020-ORD-896, Project TB5-0002(5).

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Absorption Band Systems of SiO and GeO in the Schumann Region

H. C. ROWLINSON AND R. F. BARROW

Physical Chemistry Laboratory, Oxford University, Oxford, England

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ABSORPTION bands of SiO and GeO in the region 1250-2000A have been photographed on a 1-m normal incidence grating instrument with a reciprocal dispersion of about 8.5A/mm. A Lyman discharge was used as source of continuous radiation. The SiO systems were obtained by heating mixtures of Si and SiO₂ to temperatures in the range 1200-1500°C; the GeO bands were obtained by heating solid GeO to 750-800°C.

The vibrational analyses of two systems of red-degraded bands of each molecule have so far been completed. The constants for the states of these molecules now known are given in Table I. For both molecules, the strong bands of the E-X systems are

TABLE I. Constants for the electronic states of SiO and GeO.^a

State	SiO			GeO		
	ν_e	ω_e	$X_e\omega_e$	ν_e	ω_e	$X_e\omega_e$
F	68 562.6	1114.4	7.2	67 474.4	809.0	5.66
E	52 863.2	675	4.18	50 137.4	498.7	5.3
D	42 835.3	848.5	5.84	37 767	650.4	4.21
X	0	1242.0 ₃	6.047	0	985.5	4.29

^a The constants for the states X have been taken from Herzberg (see reference 1); for the D state of SiO from Drummond (see reference 2); for the D state of GeO from Drummond and Barrow (see reference 3).