they are the most favorable structures from an energetic point of view. Consequently, the need of a complete X-ray analysis—giving bond distances and Fourier maps—is quite obvious.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Photolysis of Chloroketones[1]

BY R. P. TAYLOR AND F. E. BLACET

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An exploratory study has been made of the photolysis of 3-chloro-2-butanone and 4-chloro-2-butanone. The α-chloro compound, although thermally more unstable, gave results analogous to those obtained for chloroacetone[2] with chlorine atoms being formed in the principal primary process. The β-chloro compound appears to have more carbon–carbon bond dissociation in the primary process analogous to methyl ethyl ketone. Both compounds are thermally unstable, and their photolyses were accompanied by formation of polymeric substance.

Strachan and Blacet[2] have investigated the photolysis of chloroacetone at 3130 Å. and found good evidence that the main primary process is

$$\mathrm{CH_3COCH_2Cl} + h\nu \longrightarrow \mathrm{CH_3COCH_2} + \mathrm{Cl} \tag{1}$$

In order to compare differences in the primary process between compounds with a chlorine atom α and β to the carbonyl group, a brief study has been made of the photolyses of 3-chloro-2-butanone and 4-chloro-2-butanone.

Experimental

The α-chloro compound, 3-chloro-2-butanone, was prepared by the chlorination of 2-butanone.[3] The products were a 3:1 mixture of 3-chloro-2-butanone and 1-chloro-2-butanone which were separated by fractional distillation. The β-compound, 4-chloro-2-butanone, was made by addition of acetyl chloride to ethylene.[4] The compound was distilled several times through a column of 30 theoretical plates and at 54 mm. pressure of nitrogen. The boiling point of the distillate over the center fraction was steady at 61.8°, but after storing for a week at 0° under vacuum, analysis showed only 95% of the theoretical chlorine content. A sample left in contact with air at room temperature turned dark brown overnight and gave a strong odor of hydrogen chloride.

The photochemical apparatus and procedure was similar to that described previously.[2] All products were identified and analyzed with a mass spectrometer.

Results

The α-Chloro Compound, 3-Chloro-2-butanone.—All successful photolyses were performed at 150 and 3130 Å. The major product was hydrogen chloride, its quantum yield being approximately 0.5. Small amounts of 2-butanone and carbon monoxide were also detected, quantum yields being about 0.04 and 0.02, respectively. No methane or ethane was formed. The mass spectrogram gave small peaks at M/e of 140 and 142, possibly due to $\mathrm{CH_3{-}COC(CH_3){=}C(CH_3)COCH_3}$ and $\mathrm{CH_3COCH(CH_3)\text{-}CH(CH_3)COCH_3}$. A further product was a polymeric material deposited on the cell walls. Considerable quantities were deposited in attempts at runs below 150°. The polymer absorbed strongly at 3130 Å., but it was transparent at 4050 Å. and through the visible. A dark run at 150° showed hydrogen chloride was formed but in an amount only about 5% of that obtained in photolyses under similar conditions.

The β-Chloro Compound, 4-Chloro-2-butanone.—Dark runs at 70 and 150° yielded considerable quantities of hydrogen chloride and a product giving a large peak at M/e of 70, presumably methyl vinyl ketone formed by elimination of HCl from the parent compound. A few photolyses were tried at 150° in spite of the concurrent thermal decomposition. It could not be determined whether or not hydrogen chloride was a product as so much was present from the dark reaction. However, products obtained, which were not formed in the thermal process, were methane and carbon monoxide, both with quantum yields of about 0.3. Products were also found giving peaks at M/e of 62, 64 and 66 in the correct ratios expected for chloro compounds of mass 62 and 64 with isotopic contribution at 64 and 66. Considerable polymeric material was deposited on the walls apparently from polymerization of methyl vinyl ketone but no other products could be detected.

Discussion

The photolysis mechanism for the α-chloro compound seems to be similar to that for chloroacetone[2]

$$\mathrm{CH_3COCHClCH_3} + h\nu \longrightarrow \mathrm{CH_3COCHCH_3} + \mathrm{Cl} \tag{2}$$

$$\mathrm{Cl} + \mathrm{RH} \longrightarrow \mathrm{HCl} + \mathrm{R} \tag{3}$$

$$\mathrm{CH_3COCHCH_3} + \mathrm{RH} \longrightarrow \mathrm{CH_3COCH_2CH_3} + \mathrm{R} \tag{4}$$

$$\mathrm{2CH_3COCHCH_3} \longrightarrow \mathrm{CH_3COCH(CH_3)CH(CH_3)COCH_3} \tag{5}$$

The formation of HCl and 2-butanone is evidence for (2), (3) and (4). Reaction (5) would explain the detection of a small 142 peak. A second primary process (6), similar to that apparently observed for chloroacetone,[2] could account for the 140 peak by reaction (7).

$$\mathrm{CH_3COCHClCH_3} + h\nu \longrightarrow \mathrm{CH_3COCCH_3} + \mathrm{HCl} \tag{6}$$

$$\mathrm{2CH_3COCCH_3} \longrightarrow \mathrm{CH_3COC(CH_3){=}C(CH_3)COCH_3} \tag{7}$$

The very small yield of carbon monoxide and the lack of methane indicates that the breaking of carbon–carbon bonds is of small importance as a primary process for the α-chloro compound.

The results from the β-chloro compound are complicated by the presence of a large amount of dark reaction. It seems that moving the chlorine atom further from the carbonyl group considerably reduces the tendency to be lost; otherwise secondary

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[1] This work was supported by the Office of Ordnance Research.

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[3] M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **93**, 675 (1908).

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reactions analogous to those of the α-chloro compound would have led to the formation of 2-butanone. There is appreciable evidence for carbon–carbon bond rupture similar to that found for 2-butanone in the primary process.[5,6]

$$CH_3COCH_2CH_2Cl + h\nu \longrightarrow CH_3CO + CH_2CH_2Cl \quad (8)$$

The methane and carbon monoxide would be formed by the usual reactions of the acetyl radical, and the chloro compounds of mass 62 and 64 produced by disproportionation of the chloroethyl radical.

$$2CH_2CH_2Cl \longrightarrow CH_2ClCH_3 + CHCl{=}CH_2 \quad (9)$$

No peaks were found which would indicate that CH_2CH_2Cl radicals enter into direct combination.

LOS ANGELES, CALIFORNIA

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[CONTRIBUTION FROM THE RICHARD BENBRIDGE WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

Chemical Aspects of the Geiger–Müller Discharge. I. The Ethanol–Argon Counter[1a,b]

BY ROBERT W. KISER AND W. H. JOHNSTON

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The decomposition of the ethanol quench gas by the Geiger–Müller discharge in an ethanol–argon counter was investigated mass spectrometrically. The decomposition was first order with a decomposition constant of 8.55×10^{-9} per pulse, corresponding to an initial rate of 359 molecules of ethanol destroyed per electron passed. This large effective electron yield suggests the primary mechanism is electron collision in the gas phase.

Introduction

Although several authors have studied the decomposition of various organic quenching agents for "fast" Geiger–Müller counters, little has been done to elucidate the chemical reactions and the kinetics of the decomposition. Even the common ethanol–argon counter is not fully understood in terms of the chemical reactions governing the ethanol decomposition.

Farmer and Brown[2a] and Friedland[2b] have reported the occurrence of polymerization in methane counters, and Friedland[2b,3] has also reported the decomposition of ethyl acetate in a Geiger–Müller counter. Brown and Harris[4] have followed the destruction of the counting gases ethanol, ethylene, 1-butene and amyl acetate with the mass spectrometer.

Three mechanisms may be postulated for the decomposition of the quench gas: (1) dissociative recombination at the cathode,[5] (2) photoexcitation and (3) electron collision in the gas phase.

The present work describes further studies on the decomposition of the ethanol quench gas and reports that the ethanol is consumed by a first-order process with a large effective electron yield[6] corresponding to the electron collision mechanism. The decomposition constant is 1.08×10^{-17} per electron. Additional evidence is presented in substantiation of the Korff–Present theory of the Geiger–Müller discharge.[7]

Experimental

A silver-cathode Geiger–Müller counter was filled to a partial pressure of 10.0 mm. of absolute ethanol and to a partial pressure of 115.5 mm. of argon (Matheson). The absolute ethanol had been purified previously by a repeated freezing, cooling, and evacuation technique. The filled counter was fitted directly to the front manifold of a modified model 21-201 Consolidated Engineering Corporation mass spectrometer. The principal modification of the mass spectrometer consisted of replacement of the d.c. preamplifier and d.c. amplifiers by an Applied Physics Corporation model 30 vibrating reed electrometer and the inclusion of a 0-25 mv. range Brown Electronik recorder.

The counter gas was irradiated by a cobalt-60 source 1 cm. distant, such that the count rate was approximately 3×10^4 counts per minute. Two ordinary scalers in series were used to record the pulses of the Geiger–Müller tube, the first acting as the usual scaler and the second as the register. The gas was admitted to the mass spectrometer manifold at pre-determined times and analyzed at a constant manifold pressure. The results of these analyses are given in Table I. For calibration, numerous compounds were analyzed in the mass spectrometer.

By means of a DuMont Oscillograph-Record camera, type 297, attached to a model 535 Tektronix oscilloscope, photographs of the Geiger–Müller pulses were obtained. It was found that $7.95 \pm 0.46 \times 10^8$ electrons were passed in a single pulse.

Infrared spectra, obtained for the initial and used Geiger–Müller counter fillings to complement the mass spectrometric data, are shown in Fig. 1. A Perkin–Elmer model 21 infrared spectrophotometer was used for the infrared analyses.

Analysis of Spectral Data.—The peak ratio method[8] was used in the determination of composition from the mass spectral data. The method employed is analogous to that of Blears and Waldron.[9] The contribution of the heavier hydrocarbons to the mass peaks observed was considered negligible.

All peak intensities were referred to the m/e 20 peak. Since the m/e 45 and 46 peaks were due only to ethanol, the ethanol concentration was calculated immediately. Subtracting the contribution of ethanol to the entire spectrum, it was seen that only carbon dioxide contributed to the m/e 44 peak. The carbon dioxide contributions were subtracted from the entire spectrum. Then the remaining m/e 31 peak, due to methanol, was subtracted. From Fig. 1 it was seen that no ethane was present. Hence the m/e 29 peak was due to formaldehyde and was subtracted from the spectrum. Ethylene was then removed. Finally,

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(1) (a) This work was supported in part by the United States Atomic Energy Commission under Contract No. At(11-1)-166 with Purdue University. (b) Taken in part from a thesis submitted by Robert W. Kiser to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Master of Science, August, 1955.

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