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.

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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

RECEIVED SEPTEMBER 19, 1955

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.

[2] (a) E. C. Farmer and S. C. Brown, *Phys. Rev.*, **74**, 902 (1948); (b) S. S. Friedland, *ibid.*, **74**, 898 (1948).

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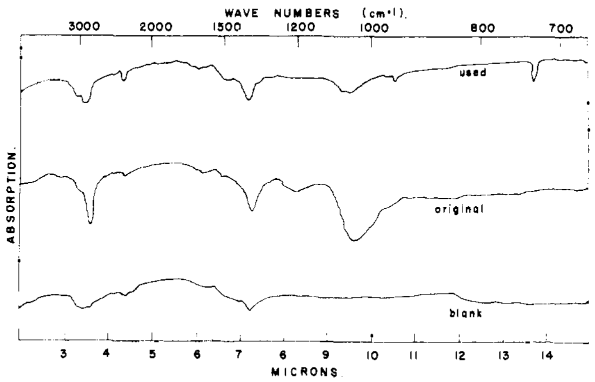

Fig. 1.—Infrared spectra.

the water spectrum, the only contribution to the *m/e* 18 peak, was subtracted, leaving the rest of the *m/e* 16 peak to be the contribution of methane. The results of these analyses of the mass spectral data are given in Table II.

TABLE I

MASS SPECTRAL DATA FOR THE DECOMPOSITION

Run →	Values in millivolts 1	2	3	4	5
Counts $\times 10^{-6}$	0	38.5	76.7	100.9	136.5
m/e					
16	0.106	0.134	0.249	0.160	0.153
17	.077	.109	0.460	.230	.106
18	.420	.450	1.83	.990	.500
20	31.66	31.485	46.08	30.27	28.2
25	0.070	0.124	0.229	0.135	0.148
26	.325	.458	1.090	0.660	0.800
27	.830	.810	1.619	0.883	1.103
28	3.633	1.450	4.78	3.37	2.645
29	0.667	0.547	1.164	0.511	0.586
30	0.297	0.093	0.293	0.112	0.135
31	3.35	2.797	4.476	1.82	2.005
40	133.66	124.97	190.94	109.92	106.899
44	0.016	0.045	0.202	0.149	0.072
45	.861	.723	1.139	.469	.411
46	.328	.264	0.457	.184	.157

TABLE II

COMPOSITION OF THE QUENCH GAS

	Moles/cc. $\times 10^9$				
Component	Run 1	Run 2	Run 3	Run 4	Run 5
Ethanol	529	337	276	218	188
Methanol	0	96.1	51.6	43.2	194
Ethylene	0	64.0	77.8	115	180
Carbon dioxide	0	1.69	17.0	29.1	12.2
Formaldehyde	0	0	0	0	0
Acetylene	0	0	3.49	1.80	0
Water	0	16.5	92.8	108	31.2
Methane	0	13.6	9.84	14.2	15.3

Results and Discussion

All peak intensities have been referred to the intensity of the *m/e* 20 peak of obtaining the ratios used in plotting Fig. 2. This figure gives a qualitative picture of the chemical aspects of the Geiger–Müller discharge. The *m/e* peak has become more intense as the number of pulses counted has increased. Table I shows that the same is true of the *m/e* 17 and 18 peaks. Therefore the formation of water and methane from the decomposition of the ethyl alcohol was postulated.

The data of Table I also show that the *m/e* 31 peak has decreased markedly and from Fig. 2 it is seen that the *m/e* 45 and 46 peaks are also decreasing, evidence that the ethanol is decomposing. The *m/e* 44 peak is increasing due to formation of the oxidation product carbon dioxide. *m/e* 25 and 26 peaks are increasing due to possible formation of ethylene and acetylene. The *m/e* 28 peak has not been considered because of its background in the mass spectrometer, largely attributable to CO^+. The *m/e* 29 peak, as seen from Table I, is only very slightly decreasing. These data coupled with the infrared data indicate that there is no formation of ethane.

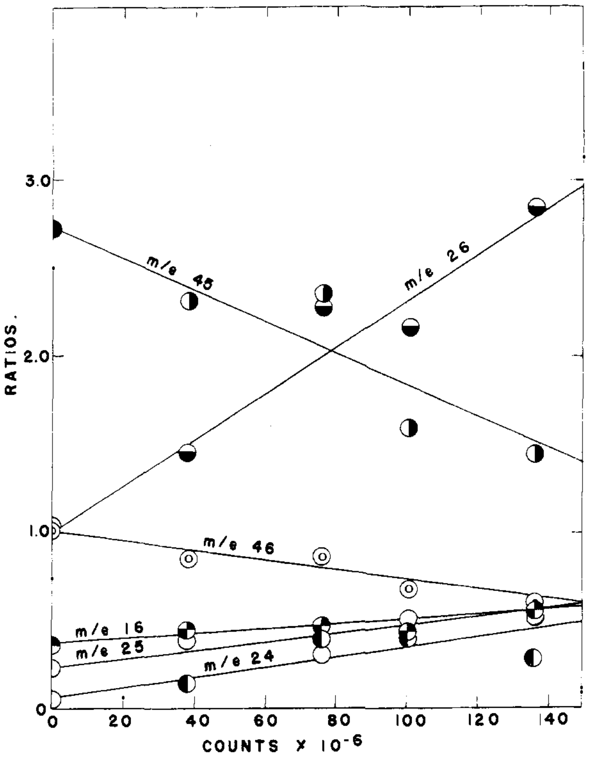

Fig. 2.—Mass peak variance.

We can conclude from these general considerations that ethanol is being decomposed and carbon dioxide, methane, water and methanol are being formed. In addition the formation of hydrogen is expected.

Analysis of the mass spectral data shows that the decomposition of ethanol is proceeding by a first-order process. The decomposition constant is found to be 8.55×10^{-9} per pulse.

Friedland[3] noted that he found a linear relation between the amount of decomposition and the number of counts in his work with ethyl acetate. However, the ratio of peak intensities cannot be construed as showing the actual amount of decomposition. Upon analysis of the mass spectral data there was found no simple linear relation between concentration of each species and the number of counts.

The photosensitivity of the cathode was found to increase with continued use, as Korff and Krumbein[10] reported. Also it was noted that during the course of this study the plateau length decreased and the slope of the plateau increased.

(10) S. A. Korff and A. D. Krumbein, *Phys. Rev.*, **76**, 1412 (1949).

At 3.85 × 10^7 counts, an average of 359 molecules of ethanol were destroyed per electron. After 1.365 × 10^8 counts the average effective yield for ethanol was 180, since the products being formed were also being decomposed in the discharge. The mechanism of dissociative recombination whereby an organic molecule is neutralized at the cathode by an electron and dissociates from the excitation of ion recombination is expected to have an effective electron yield of approximately unity. If the mechanism of decomposition were photoexcitation, where the electron transfer between an argon ion and a molecule of the organic quenching agent produces a photon which is then absorbed by another organic molecule to give an excited intermediate, the effective electron yield is again expected to be unity. But the mechanism of electron collision in the gas phase, in which an electron collides with an organic molecule in traveling to the anode and loses some of its energy in excitation of the molecule, but which in being accelerated toward the anode acquires more energy for another collision, must have an effective electron yield much greater than unity. The primary mechanism, considering the large observed effective electron yield, is concluded to be that of electron collision in the gas phase.

Stating the mechanism of electron collision in terms of an equation

$$CH_3CH_2OH + \bar{e} \xrightarrow{\text{gas}} (CH_3CH_2OH)^+ + \bar{e}$$

it is seen then that the subsequent steps may be any or all of the following

$$(CH_3CH_2OH)^+ \longrightarrow \cdot CH_3 + \cdot CH_2OH$$
$$(CH_3CH_2OH)^+ \longrightarrow \cdot CH_2CH_3 + \cdot OH$$
$$(CH_3CH_2OH)^+ \longrightarrow \cdot C_2H_4OH + \cdot H$$

Various propagation and termination steps may then be written involving free radical reactions. In a system of this kind it is clear that many reactions are possible. The stoichiometry of the observed decomposition, as seen from Table II, may be approximated by

$$24CH_3CH_2OH \longrightarrow 16CH_3OH + 15C_2H_4 + CH_4 + CO_2 + H_2 + 6H_2O$$

The authors wish to thank Mr. R. W. Hannah for the infrared analyses.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions in Complex Ions. VII. Base Hydrolysis of Some Cobalt(III) Complex Ions[1,2]

BY RALPH G. PEARSON, ROBERT E. MEEKER AND FRED BASOLO

RECEIVED OCTOBER 11, 1955

The rates of base hydrolysis of a number of inorganic coördination complexes such as *cis*- and *trans*-dichlorobisethylenediaminecobalt(III) chloride have been determined. These reactions are quite rapid, generally having half-times of fractions of a second at room temperature. A simple flow apparatus utilizing electrical conductivity measurements for fast reactions is described. From the effect on reaction rate of various structural modifications in the complex molecule, an S_N1CB mechanism is proposed in which the reaction proceeds by dissociation of a chloride ion from the conjugate base of the complex cation. This mechanism is consistent with the expected acidities and rates of dissociation of the various complex ions. The data are correlated by applying the rule that rates of base hydrolysis should parallel rates of acid hydrolysis for a series of complex ions of cobalt(III) unless a marked change occurs in the acidities of some members of the series.

The mechanism of base hydrolysis of complex ions such as

$$[Co(NH_3)_5Cl]^{+2} + OH^- \longrightarrow [Co(NH_3)_5OH]^{+2} + Cl^- \quad (1)$$

has been considered by Brown, Ingold and Nyholm[3] to be a direct displacement of halide ion by hydroxide ion (an S_N2 process). This is in agreement with the observed kinetics of such reactions which are first order in hydroxide ion and first order in complex ion.

Others[4] have considered the mechanism to involve a prior acid–base equilibrium followed by release of halide ion from the conjugate base of the complex cation (an S_N1CB process).

$$[Co(NH_3)_5Cl]^{+2} + OH^- \underset{\text{fast}}{\rightleftarrows} [Co(NH_3)_4NH_2Cl]^+ + H_2O \quad (2)$$

$$[Co(NH_3)_4NH_2Cl]^+ \xrightarrow[\text{slow}]{H_2O} [Co(NH_3)_4NH_2H_2O]^{+2} \xrightarrow[\text{fast}]{} [Co(NH_3)_5OH]^{+2} \quad (3)$$

This mechanism is in agreement with the recent observation that complexes containing no acidic protons release their replaceable ligands at a rate independent of the *p*H of the solution.[5] In such compounds step (2) cannot occur.

The way in which water replaces chloride ion in step (3) is presumably the same as for aquation of the parent ion under acid conditions (acid hydrolysis).

$$[Co(NH_3)_5Cl]^{+2} + H_2O \longrightarrow [Co(NH_3)_5H_2O]^{+3} + Cl^- \quad (4)$$

Earlier papers in this series[1,7] have reported the rates of acid hydrolysis as in (4) for a large number of complex ions of cobalt(III). Evidence has been presented to show that (4) probably involves a dissociation mechanism (S_N1) in which a pentacoördinated intermediate is formed.

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[1] Previous paper in this series, R. G. Pearson, P. M. Henry, J. G. Bergmann and F. Basolo, THIS JOURNAL, **76**, 5920 (1954).

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