of this reaction is due to a large entropy of activation involving a complex orientation and solvation of the activated complex[12] and probable solvation of the iodobenzene in water in the manner of Baker's observations of 12 water molecules per molecule of octadecane in water.[13]

[12] W. F. K. Wynne-Jones and H. Eyring, *J. Chem. Phys.*, **3**, 497 (1935).

[13] E. G. Baker, "Symposium on Chemistry in the Exploration and Production of Petroleum," American Chemical Society, Dallas Meeting, April, 1956.

LAFAYETTE, IND.

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

Chemical Aspects of the Geiger–Müller Discharge. II. The 2-Propanol–Argon Counter[1]

BY ROBERT W. KISER AND W. H. JOHNSTON

RECEIVED SEPTEMBER 4, 1956

The decomposition of 2-propanol quench gas by the Geiger–Müller discharge in an argon counter was investigated mass spectrometrically. Decomposition is essentially first order with a decomposition constant of 2.63×10^{-9} per pulse. The stoichiometry for the observed decomposition of 2-propanol may be approximated by $14CH_3CH(OH)CH_3 = 9CH_3CH_2OH + 8CH_3CHCH_2 + 5H_2O$. The primary mechanism of decomposition is attributed to electron impact in the gas phase. The specific electron yield is determined for 2-propanol and compared with the previously studied case of ethanol.

Introduction

In an attempt to elucidate the chemical reactions and the kinetics of decomposition of the quenching agent in a Geiger–Müller counter, Kiser and Johnston recently reported a study of the ethanol–argon counter.[2] Of the three mechanisms postulated, the primary mechanism of decomposition was that of electron impact in the gas phase.

It is of interest to know whether this mechanism also is dominant for other quenching agents. The present work describes a study of the decomposition of the quenching agent 2-propanol, where it is evidenced that the electron impact mechanism still predominates. The 2-propanol decomposition in argon has a first-order decomposition constant of 1.17×10^{-18} per electron.

The effective electron yield of the decomposition of 2-propanol and of the previous case of ethanol were recalculated in the form of specific electron yields for decomposition. A simple qualitative explanation is given for the difference between these yields.

Experimental

A Geiger–Müller counter with an internal silver cathode was filled to a partial pressure of 9.1 mm. with 2-propanol vapor and to a partial pressure of 82.9 mm. with argon (Matheson). The 2-propanol previously had been purified by repeated freezing and evacuation. This counter was then fitted directly to the front manifold of a modified model 21-201 Consolidated Electrodynamics Corporation mass spectrometer. The modifications of the mass spectrometer employed have been described previously.[2]

The source of radiation was cobalt-60 of approximate strength of 10 microcuries, placed 2.5 cm. distant from the counter wall. The count rate was approximately 2×10^4 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 at varying times and analyzed at a constant manifold pressure. Because of time limitations during analyses, the region observed ranged from *m/e* 19 to *m/e* 59. The results of these determinations are given in Table I.

Although the mechanism does not appear to be the same for the methane counter,[3,4] it is possible that the electron impact mechanism may operate in the case of ethyl acetate.[4,5,6]

TABLE I

MASS SPECTRAL DATA FOR THE DECOMPOSITION (CORRECTED), VALUES IN MILLIVOLTS

Counts $\times 10^{-6}$ *m/e*	0	8.76	20.2	32.9	56.2	68.0	68.8
20	33.3	34.3	36.4	35.2	35.8	38.3	43.5
26	0.51	0.36	0.32	0.36	0.38	0.39	0.44
27	1.96	1.86	1.55	1.66	1.58	1.58	1.94
28	4.48	3.50	3.23	3.48	3.60	3.96	5.15
29	0.93	0.80	0.80	0.72	0.72	0.76	0.90
31	.81	.53	.52	.57	.54	.64	.71
32	.00	.11	.08	.06	.05	.03	.05
39	1.03	.88	.83	1.00	1.04	1.07	1.24
40	119.0	125.0	119.9	125.4	124.9	129.0	147.0
41	1.35	1.12	1.12	1.26	1.33	1.36	1.60
43	1.20	1.09	0.95	1.01	1.04	1.07	1.21
44	0.31	0.28	0.23	0.25	0.21	0.26	0.30
45	5.31	4.47	4.17	4.43	4.19	4.13	4.69

For maintenance of a continual check on the sensitivity of the mass spectrometer during these analyses, a reference gas mixture composed of argon, ethene, ethanol and 2-propanol also was analyzed regularly. The seven analyses performed on the synthetic reference gas mixture agreed to within 4%, the major peaks having only a disagreement of 1 to 1.5%. The argon content of the counter remained constant to within 1%. The analysis of the synthetic gas mixture agreed to within an average deviation of about 5% from the manometric data obtained from the blending process. By a comparison of each individual analysis of the reference gas mixture with the average of all such analyses, values were obtained with which to correct the mass spectrum of each analysis of the 2-propanol–argon counter filling. This compensated for the greatest part of noted fluctuations in the mass spectrometer during analyses. To obtain calibrations, the pure gases and vapors were analyzed separately.

By means of the technique described in the earlier work on ethanol,[2] it was found that $(2.25 \pm 0.13) \times 10^9$ electrons are passed in each pulse counted in the 2-propanol–argon counter.

Analysis of Spectral Data.—The detailed method for the determination of the composition from the mass spectral

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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 work in progress for a thesis to be submitted by Robert W. Kiser to the Graduate School of Purdue University in partial fulfillment of the requirements for the Ph.D. degree.

[2] R. W. Kiser and W. H. Johnston, THIS JOURNAL, **78**, 707 (1956).

[3] E. C. Farmer and S. C. Brown, *Phys. Rev.*, **74**, 902 (1948).

[4] S. S. Friedland, *ibid.*, **71**, 377 (1947).

[5] S. S. Friedland, *ibid.*, **71**, 898 (1948).

[6] S. S. Friedland and H. S. Katzenstein, *ibid.*, **84**, 591 (1951).

data[7,8] is as follows: All corrected peak intensities were referred to the *m/e* 40 peak. The *m/e* 40 peak was chosen as the basis of reference because it was the largest peak and therefore introduces the smallest background errors. Since the *m/e* 32 peak is due only to methanol, the methanol contribution was calculated immediately. After subtracting the contribution of the methanol from the unknown spectrum it is seen that the *m/e* 31 peak is due only to ethanol. The ethanol contribution to the spectrum was subtracted. The remaining *m/e* 45 peak, due only to the contribution of 2-propanol, was subtracted, after which the remaining *m/e* 41 peak, attributed only to propene, was subtracted. Then the *m/e* 20 peak is due essentially to argon. Subtraction of the argon contribution, followed by subtraction of the propyne contribution as indicated by the *m/e* 40 peak, gave a resultant spectrum composed essentially of ethene, ethyne, methanal, ethanal, propane and carbon dioxide. The *m/e* 39 peak, due to propane, was calculated and the propane contribution subtracted. Then the *m/e* 43 peak was considered to be due only to ethanal, and its contribution was removed. Carbon dioxide then constitutes all of the remaining *m/e* 44 peak. Assuming no presence of ethane[9] in the decomposition products, the *m/e* 29 peak is then due singularly to methanal. After subtraction of the methanal contribution, the *m/e* 27 peak is due only to ethene. Finally, upon subtraction of the ethene contribution, ethyne was calculated from the *m/e* 26 peak intensity.

The composition was obtained from the mass spectral data in a more rigorous manner, involving the solution of the appropriate determinants. These results and the results from the subtraction technique have been taken together to give "acceptable solutions." The results of the analyses computed in this manner are given below.

Results

It is observed in referring to Table I that the intensities of the argon peaks, *m/e* 20 and *m/e* 40 corresponding to A^{++} and A^{+}, have remained constant, as is to be expected. However, it is also noted that the intensities of the *m/e* 27, 29, 31, 41 and 43 peaks have decreased. In addition, other peaks show variable trends which can only be analyzed correctly when the entire set of data is analyzed for the individual components.

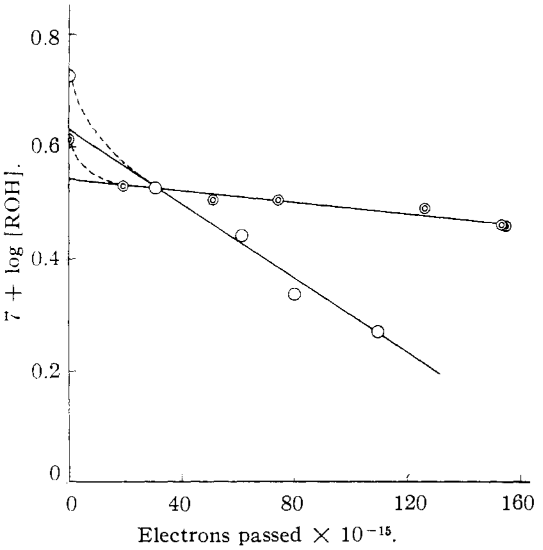

Fig. 1.—Decomposition of ethanol and 2-propanol in the Geiger counter: O, ethanol; ◎, 2-propanol.

The analysis of the mass spectrometric data of Table I, as outlined above, yielded the following results: (1) no ethene, ethyne, propane, propyne, methanol, methanal, ethanal nor carbon dioxide was present in any of the seven analyses; (2) the argon concentration remained constant at 450 × 10^{-8} mole/cc. over the seven analyses; (3) the 2-propanol concentration decreased from 41 to 34 to 32 to 32 to 30.9 to 29.0 to 28.9 × 10^{-8} mole/cc. in the seven analyses; (4) the ethanol concentration increased from 0 to 5.3 to 5.7 to 6.1 to 6.1 to 8.1 to 7.7 × 10^{-8} mole/cc. in the seven analyses; and (5) the propene concentration increased from 0 to 3.6 to 5.1 to 6.0 to 7.2 to 7.5 to 8.0 × 10^{-8} mole/cc. in the seven analyses.

It is thus observed that the 2-propanol is being decomposed and that ethanol and propene are being formed as decomposition products of the 2-propanol. Peaks below *m/e* 19 were not scanned; however, water vapor is to be expected among the decomposition products. The decomposition of the 2-propanol quench gas in the Geiger–Müller counter in the presence of argon is shown in Fig. 1.

In both the present case of 2-propanol and in the previous study of ethanol there is an initial loss which is attributed to adsorption and which was eliminated in obtaining the first-order decomposition rates shown in Fig. 1. This represents an improvement in the value for ethanol as compared with the value reported previously.

Table II summarizes the comparisons between ethanol and 2-propanol as quench gases in these studies of Geiger–Müller counters containing argon.

TABLE II

COMPARISON OF ETHANOL AND 2-PROPANOL

	Ethanol	2-Propanol
Filling (at 298°K.)		
Argon, mm.	115.5	82.9
ROH, mm.	10.0	9.1
Counter vol., ml.	95	95
Cathode	Ag	Ag
Electrons pulse^{-1} × 10^{-9}	0.795 ± 0.045	2.25 ± 0.13
$k \times 10^{18}$	7.49	1.17
X_0 mm. ROH (at 298°K.)	8.04	6.46
Normal modes of vibration	21	30
S	285	55.5

The number of electrons passed in each discharge of the Geiger–Müller counter was observed to be (2.25 ± 0.13) × 10^9. This value is nearly three times as great as the corresponding value for ethanol. However, both the ethanol and the 2-propanol values are of the order of magnitude quoted by Korff.[10] The decomposition constant for the 2-propanol, as seen from Fig. 1 and from Table II, is smaller than that for ethanol by a factor of approximately six. The specific electron yield, to be discussed below, is about one fifth as large in the case of the 2-propanol. The increase in number of electrons passed per pulse and the de-

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(7) A. J. B. Robertson, "Mass Spectrometry," Methuen and Co., Ltd., London, 1954, pp. 84–101.

(8) G. P. Barnard, "Modern Mass Spectrometry," Institute of Physics, London, 1953, pp. 214–229.

(9) The absence of ethane in the products of the decomposition of ethanol in the Geiger–Müller discharge was established in previous work. Therefore it is not unreasonable to make this assumption in this case where, from the mass spectral data of 2-propanol, it is seen that ethane formation is still less probable than with ethanol.

(10) S. A. Korff, "Electron and Nuclear Counters," Second Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1955, pp. 139, 155.

crease in the decomposition constant couple to reduce the specific electron yield in the 2-propanol study.

Discussion

Although the effective electron yield was previously defined as $\Delta x/\Delta\epsilon$, it would appear better to speak of an instantaneous effective electron yield, $-dx/d\epsilon$, which is a linear function of X, the number of molecules of quench gas. We define a specific electron yield, S, as the constant relating these quantities. We define the standard state, for calculation of S, as 10.00 mm. pressure of quench gas at 298°K. This provides a comparison of the specific electron yield of various quenching agents at different partial pressures. The calculated values of S for ethanol and 2-propanol are given in Table II.

In attempting to explain the difference in specific electron yield between ethanol and 2-propanol we consider that the majority of decomposition occurs by dissociation of alcohol molecules in primary excitation by electron collision. As may be seen from Table II, there are half again as many normal modes of vibration for 2-propanol as there are for ethanol. Qualitatively it is therefore not unreasonable that fewer excited molecules of 2-propanol undergo dissociation, giving a lower value of the specific electron yield in the case of the 2-propanol–argon Geiger–Müller counter.

The useful life of the counter filling is somewhat shorter than would be expected solely on the basis of decomposition of the quench gas. This at first appears strange inasmuch as the quenching agent ethanol is a product of this decomposition and should lengthen the life of the counter filling. However, the water produced in the decomposition is electron-attaching and thus seriously shortens the expected lifetime of the counter filling.

From the large value of electron yield it is concluded that the primary mechanism for the decomposition of 2-propanol, as with ethanol, is that of electron impact in the gas phase. This decomposition of 2-propanol, controlling the useful life of the 2-propanol–argon Geiger–Müller counter, may be expressed approximately in terms of the stoichiometric equation

$$14CH_3CH(OH)CH_3 = 9C_2H_5OH + 8CH_3CHCH_2 + 5H_2O$$

It is interesting to speculate that many reactions of radiation chemistry probably proceed by this type of excitation independently of ion recombinations.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

Decomposition of Ethylene in an Electric Discharge[1]

BY M. PRAKASA REDDY[2] AND MILTON BURTON

RECEIVED JUNE 28, 1956

The effects of an atmospheric pressure electric discharge on C_2H_4 as well as on mixtures of C_2H_4 with H_2, D_2, H_2 plus D_2, C_2H_2, C_2D_2 and C_2D_4, respectively, have been studied. The products formed are compared with those produced from low pressure discharge through C_2H_4 as well as with those formed by bombardment with 1.5 Mev. electrons. The rate dependence of the over-all reaction $C_2H_4 \rightsquigarrow C_2H_2$, etc., in the atmospheric pressure discharge through pure C_2H_4, is first-order in C_2H_4 and apparently half order in current. Carbon production is suppressed by initial admixture of H_2 or D_2. The reaction appears to proceed by successive removal of H atoms (not of a single H_2 molecule in an elementary process). The calculated average energy of the electrons is of the order of 1 e.v. and it is suggested that a successive excitation mechanism is required to maintain the discharge. The half-order dependence on current may be an artifact resultant from the fact that in an unconstricted discharge the current density tends to remain constant. It is shown that a kinetic scheme which depends on Stern–Volmer reactions of excited C_2H_3 appears to afford the most satisfactory interpretation of the totality of the results.

1. Introduction

The current view of the chemical effect of an electric discharge derives essentially from Emeleus and Lunt[3,4] who emphasized the role of excitation (as distinguished from ionization) and treated the phenomena as rate processes proceeding through the intermediary of free radicals.[4] Recent experimental and theoretical work has tended to support these views. Wiener and Burton[5] interpreted Schoch's results on methane in an atmospheric pressure discharge[6] in terms of the dominant role of a free radical species, perhaps CH_2.[7] Schoch has shown that ethylene also yields acetylene with high efficiency in the electric discharge; he reports a maximum yield of 15 C_2H_2 molecules per 100 e.v. input; *i.e.*, $G(C_2H_2) = 15$.[6b] The work here reported was undertaken with the purpose of elucidation of the factors which give rise to such high efficiency under the apparently diverse situations represented by methane and ethylene.

2. Experimental

2.1. Chemicals.—Ethylene supplied by the Matheson Co., containing butene and ether up to a maximum of 1%, was purified by slow circulation through a spiral cooled at −100°. Hydrogen was Matheson electrolytic grade.

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[1] Contribution from the Radiation Project of the University of Notre Dame, supported in part under U. S. Atomic Energy Commission contract At(11-1)-38 and U. S. Navy equipment loan contract Nonr-06900. This paper is an abstract from a thesis presented by M. P. Reddy in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Notre Dame.

[2] Olin Research Fellow at the University of Notre Dame during most of the work reported. This work was also assisted by an additional grant from the Olin–Mathieson Chemical Corporation.

(3) R. W. Lunt and K. G. Emeleus, *Nature*, **137**, 404 (1936).

(4) K. G. Emeleus and R. W. Lunt, *Trans. Faraday Soc.*, **32**, 1504 (1936).

(5) H. Wiener and M. Burton, THIS JOURNAL, **75**, 5815 (1953).

(6) (a) E. P. Schoch, *et al.*, University of Texas Publication, No. 5011, "Acetylene from Hydrocarbons," June 1, 1950; (b) private communications.

(7) M. Burton and J. L. Magee, *J. Chem. Phys.*, **23**, 2195 (1955).