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Precise Measurements of W , the Average Energy Required for Ion Pair Formation. II. Alcohols and Water¹

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Ionization currents produced in simple alcohols by the decay of ^{63}Ni were measured with a reproducibility of about 0.01% at approximately 100 and 200° and over a pressure range of from 600 to 2500 Torr. In methanol and ethanol extrapolated and normalized ionization currents appear to decrease by approximately 5% over this range; this is ascribed to incomplete ion collection by applying a criterion for the attainment of saturation based on an analysis of slopes of current *vs.* potential curves. The following values of W relative to $W(\text{N}_2) = 34.6$ were obtained in the lower pressure range where ion collection is essentially complete: $W(\text{H}_2\text{O}) = 29.15 \pm 0.09$, $W(\text{CH}_3\text{OH}) = 25.02 \pm 0.09$, $W(\text{C}_2\text{H}_5\text{OH}) = 24.50 \pm 0.09$, $W(n\text{-C}_3\text{H}_7\text{OH}) = 23.86 \pm 0.08$, $W(i\text{-C}_3\text{H}_7\text{OH}) = 24.25 \pm 0.09$, $W(n\text{-C}_4\text{H}_9\text{OH}) = 23.53 \pm 0.12$, $W(2\text{-C}_4\text{H}_9\text{OH}) = 23.53 \pm 0.12$, and $W(i\text{-C}_4\text{H}_9\text{OH}) = 23.38 \pm 0.11$ eV per ion pair.

Introduction

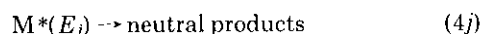
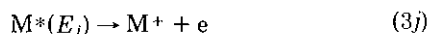
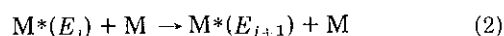
The improvement of our insight into elementary processes in radiation chemistry, an endeavor which has made forceful strides as a result of the devotion of Professor M. Burton to this field, requires a continual reduction of the time span covered by the prime radiation chemical symbol, the wiggly arrow introduced by Burton. Modern pulse techniques are able to penetrate the picosecond range,² but details of the ionization process involving iso-

lated molecules and their interaction with high-energy radiation are as yet not accessible.

Information on the ionization process can also be ob-

- (1) Presented as part of a plenary lecture on "Ionization of Gases by High Energy Radiation" at the International Conference on Elementary Processes of Radiation Chemistry, held in honor of the 70th birthday of Professor Milton Burton at the University of Notre Dame, April 4-7, 1972.
- (2) J. E. Aldrich, M. J. Bronskill, R. K. Wolff, and J. W. Hunt, *J. Chem. Phys.*, **55**, 530 (1971).

tained from the study of gross ionization in gases. Particularly the investigation of mixtures,³⁻⁷ primarily using α -ray ionization chambers,⁴⁻⁷ has resulted in a considerable increase of our understanding of second-order ionization processes and of the role and yield of excited states in the rare gases. These states are relatively long-lived or represent trapped resonance radiation. This kind of investigation has, however, not provided information on fast first-order ionization processes with picosecond lifetimes. At least in principle, this time range should be accessible from data on the change in the rate of ionization with pressure. For example, collisions may affect the branching between preionization and predissociation of a superexcited state⁸ $M^*(E_j)$ with energy E_j greater than the ionization potential (I.P.) in a mechanism which may be summarized as



where reaction 2 removes energy from excited intermediates to yield states of lower excitation energy (E_{j+1}), etc.; k_{3j}/k_{4j} is a function of E_j , possibly discontinuous, and is obviously zero for $E_j < \text{I.P.}$ Provided that the lifetime of the $M^*(E_j)$ states is sufficient, increased gas density will effect a reduction in the mean excitation energy $\langle E_j \rangle$. Presumably $\langle k_{3j}/k_{4j} \rangle$ will decrease as $\langle E_j \rangle$ decreases since $k_{3j} = 0$ for $E_j < \text{I.P.}$; one can express the effect of this change in the probability distribution of excitation energies by recognizing the dependence of the distribution on density ρ , i.e., $P(E_j, \rho)$. Denoting the yield of all superexcitation processes as G_s and that of all direct ionization processes as G_d , the yield of ions in this formalism is

$$G_{\text{ions}} = G_d + G_s \sum_{E_j=\text{I.P.}}^{\infty} [k_{3j}(E_j)/[k_{3j}(E_j) + k_{4j}(E_j)]P(E_j, \rho)] \quad (A)$$

If only a single state ss were involved and if the first collision always were to cause a reduction of E_j to $E_{j+1} < \text{I.P.}$, the familiar expression

$$G_{\text{ions}} = G_d + G_{ss}[k_3/k_2[M + k_3 + k_4]] \quad (B)$$

would result. In any event, the change in ionization yield with density arises through $P(E_j, \rho)$.

Even if such a mechanism should be operative, preionization lifetimes could not be assessed directly because the rate constant of reaction 2 cannot be estimated directly from collision theory. Not only may not all collisions be strongly deactivating,⁹ but the collision diameter of the species M^* is uncertain. Molecular autoionizing states are largely high-lying Rydberg series^{10,11} with mean radii considerably greater than those of molecules in their ground electronic state. However, an effective deactivating collision should require interaction with the core to remove vibrational energy. Since the mean of the radial distribution function of Rydberg states decreases with increasing n , that is, the wave function becomes spread over a larger volume, the collision may also be approximated as occurring between a quasi-ion and a neutral molecule to give an upper limit to the rate constant.

In order for such a mechanism to manifest itself, autoionization rates must be sufficient to be detectable

within the precision of the method. The first criterion seems to be fulfilled since theoretical considerations¹⁰⁻¹² have indicated that autoionization lifetimes in hydrogen should be in the range of 10^{-8} to 10^{-12} sec, and the magnitude should be comparable for more complex molecules particularly since lifetimes approach infinity, for transitions involving the same initial and final vibrational states, as the principal quantum number increases.^{11,12} Yields, however, are probably small.

Recently Brehm, *et al.*,¹³ have reported photoionization studies which suggest strongly that autoionization may be a substantial contributor to overall ionization in methanol and ethanol. Therefore, we have measured precise ionization rates in a series of alcohols and have investigated the dependence of total ionization currents in methanol on pressure between 600 and 2500 Torr at 200°, corresponding to collision-free periods of from 3 to 11×10^{-11} sec at the lower pressure and 0.8 to 2.8×10^{-11} sec at the higher pressure depending on whether one assumes a collision of hard spheres having molecular dimensions, or regards the collision as the interaction of a quasi-ion with a neutral molecule and employs the experimental ion-molecule reaction rate constant of $2.5 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$ for reaction of CH_3OH^+ with CH_3OH .¹⁴

Experimental Section

Ionization produced by decay of ^{63}Ni plated on the central section of a parallel nickel wire grid, of 0.005-in. diameter, centered in a spherical chamber was measured as a function of applied voltage using a current to frequency converter by determining the period elapsed during the accumulation of a preset count. Details of the apparatus and procedure have been reported previously.¹⁵ Minor changes included potting of the external portion of the triaxial feedthrough with General Electric RTV silicone resin to reduce arcing, and replacement of the mercury manometer with a Heise Model CMM-6, 0-4000-Torr pressure gauge accurate to 0.1% and reproducible to 0.02%.

All alcohols were the purest grade available from Matheson Coleman and Bell and were distilled on a 1 m \times 1-cm glass bead column, the middle one-third being retained. Water was distilled from permanganate solution. Samples were degassed by pumping on the liquid at ambient temperature immediately prior to vaporization and introduction into the sample handling system.

Results

1. *Relative Ionization in Alcohols.* Contrary to earlier observations in hydrocarbons and nitrogen,¹⁵ where the

- (3) (a) W. P. Jesse, *J. Chem. Phys.*, **41**, 2060 (1964); (b) W. P. Jesse and R. L. Platzman, *Nature (London)*, **195**, 790 (1962).
- (4) G. S. Hurst, T. E. Bortner, and R. E. Glick, *J. Chem. Phys.*, **42**, 713 (1965).
- (5) T. D. Strickler, *J. Phys. Chem.*, **67**, 825 (1963).
- (6) C. E. Klotz, *J. Chem. Phys.*, **44**, 2715 (1966).
- (7) L. M. Hunter and R. H. Johnson, *J. Phys. Chem.*, **71**, 3228 (1967).
- (8) R. L. Platzman, *Vortex*, **23**, (8), 372 (1962).
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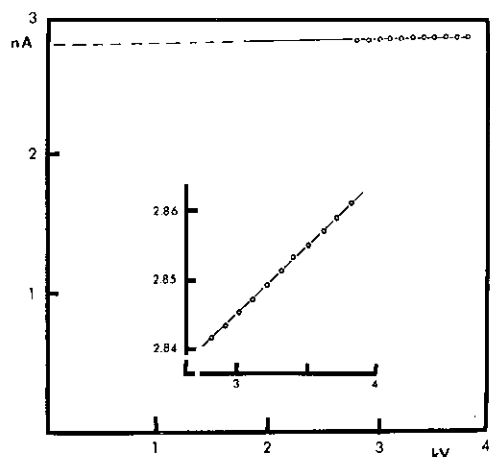


Figure 1. Variation of observed collector current i with applied potential. The insert is an expanded section and point size corresponds to approximately 0.01% of the ion current (isobutyl alcohol, 203°, 907 Torr).

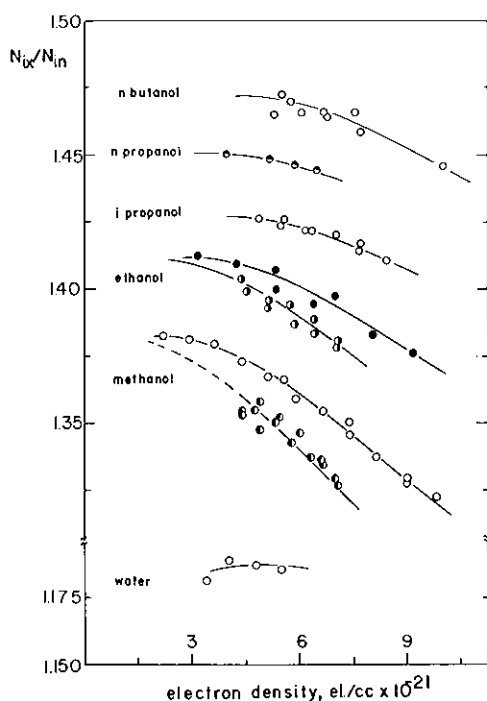


Figure 2. Variation of extrapolated ion current (N_{ix}) normalized to the extrapolated ion current in nitrogen at the same electron density (N_{in}) with electron density. Top to bottom: 1-butanol, 213°; 1-propanol, 236°; 2-propanol, 193°; ethanol, 203°; ethanol, 123°; methanol, 204°; methanol, 118°; water, 240°.

dependence of ion current on voltage is linear above 1–1.5 kV, apparent linearity was observed for the alcohols only at higher voltages. While the reproducibility of individual points was on the order of 0.005% and their deviation from a straight line in the region used for extrapolation was within the same magnitude, least-squares analysis of the data to assess the intercept showed typical standard deviations of the intercept to be 0.02 to 0.06%. An example of the saturation curve and the precision attainable are shown in Figure 1 for 2-methyl-1-propanol (isobutyl alcohol) at 203° and 907 Torr.

Intercepts obtained by this procedure (N_{ix}) were compared to those obtained on the same day for nitrogen at

the same electron density (N_{in}) over a range of pressures and for methanol and ethanol, at two temperatures. Since errors which may result from incomplete energy loss of the β particle and back-scattering should be roughly related to electron density of the sample and to a lesser extent to the effective atomic number, our results are presented in Figure 2 as a function of electron density. Not shown are results for isobutyl alcohol which are nearly superimposable on those for 1-butanol and those for 2-butanol.

It is apparent that the relative extent of ionization decreases with increasing pressure or electron density for all alcohols, although the degree of dependence varies. No such variation was observed for alkanes over an even larger range of electron densities.¹⁵ It was necessary therefore to investigate the possibility that this variation is an artifact resulting from incomplete ion collection which does not manifest itself in a deviation from linearity of current vs. voltage plots.

2. *Criterion for Total Ion Collection.* The apparent ion current can be expressed as the sum of a series of contributions, which include a resistive component R in the feedthrough assembly, and a number of energy terms: the mean effective β -ray energy, E_β , the energy associated with back-scatter into the grid wires, E_{BS} , that which is lost to adjacent wires or the chamber walls (E_{geom}), and energy gained (or lost) by electrons under the influence of the collecting field (E_{field}). In addition, total ion pair formation resulting from the energy terms may be reduced by incomplete collection and increased by ion multiplication. The ion current i is related to these parameters by the equation

$$i = \frac{V}{R} + \frac{DF}{N_A W} (E_\beta - E_{BS} - E_{geom} + E_{field}) f M \quad (1)$$

where N_A is Avogadro's number, V is the applied potential, F is Faraday's constant, and D is the rate of disintegration of ^{63}Ni . W is the average energy per ion pair and is assumed to be independent of the source of energy, while f is the collection efficiency and M is the ion multiplication factor.

The first three energy terms do not affect relative measurements at the same electron density, while the energy gained by the field should be approximately proportional to the applied potential and the range of the electron.¹⁶ Since the range is inversely proportional to electron density ρ , one may write

$$E_{field} = \frac{cV}{\rho} \quad (II)$$

where c is a proportionality constant.

The collection efficiency has been analyzed by Boag.¹⁷ For spherical chambers in the limit where collection is nearly complete, it can be written as

$$f = 1 - \frac{C \rho_n P^2 k_r}{T^2 K_+^0 K_-^0 V^2} \quad (III)$$

where C is a constant, k_r is the recombination coefficient, K_0 represents the reduced mobility of the positive and negative species, respectively, and P is the pressure. The exponent n of ρ may be as large as 3 and arises from the variation in mean ionization density, which increases as the cube of stopping power of the medium for a point source. For our chamber, n is probably between 2 and 3.

(16) C. Wingate, W. Gross, and G. Failla, *Radiat. Res. Res.*, **8**, 411 (1958).

(17) J. Boag in "Radiation Dosimetry," G. J. Hine and G. L. Brownell, Ed., Academic Press, New York, N. Y., 1956, Chapter 4, p 153.

The P^2 term results from the pressure dependence of the mobility.

The ion multiplication factor is related to the first Townsend coefficient $\alpha^{18,10}$ since multiplication is small

$$M = \exp(\alpha d) \approx 1 + \alpha d \quad (\text{IV})$$

Here d is the mean distance between ion pair formation and the chamber walls and somewhat, but not greatly, dependent on density since ion formation is always predominantly near the central grid structure. Substitution of the empirical form of α yields

$$M \approx 1 + APd \exp(-BP/V) \quad (\text{V})$$

where A and B are constants.

Insertion of all expressions into (I), neglect of the product of terms much smaller than unity, and combination of the first three energy terms into a net energy E_n , yields

$$i = V/R + [DF/(N_A W)](E_n + cV/\rho)[1 - C\rho^n P^2 k_r / (T^2 K_+^0 K_-^0 V^2) + APd \exp(-BP/V)] \quad (\text{VI})$$

Apparently the last two terms which allow for incomplete collection and ion multiplication are small enough not to reflect themselves in nonlinearity of plots of i vs. V . However, the extrapolation occurs over a substantial range, and even relatively minor systematic errors in the slope will amplify themselves in the extrapolation procedure. The slope of N_i vs. V plots should be given by the derivative of eq VI.

$$\frac{di}{dV} = \frac{1}{R} + \frac{DF}{N_A W} \left[\frac{c}{\rho} + \frac{C\rho^n P^2 k_r}{T^2 K_+^0 K_-^0 V^2} \left(\frac{c}{\rho} + \frac{2E}{V} n \right) + Ad \left(\frac{cP}{\rho} - \frac{BcP}{V} - \frac{BP^2 E}{V^2} n \right) \exp \left(-\frac{BP}{V} \right) \right] \quad (\text{VII})$$

When complications from other factors are absent, only the first two terms contribute and a plot of slope vs. $1/\rho$ should yield a straight line with intercept $1/R$ and slope $DF/(WN_A)$.

Equation VII was tested using propane as a standard; no apparent pressure effect has been observed for this gas at electron densities up to 1.2×10^{21} electrons cm^{-3} , and in fact a linear relationship is obtained over this density range (Figure 3). At high electron densities, however, even propane shows an increase in slope, and concomitant saturation ionization currents determined from intercepts decrease while W values so obtained increase. The deviation sets in at even lower electron densities in methanol and ethanol, and scatter as well as deviations from a line calculated using eq VII and the empirical values of R and c derived from the propane data are more dominant at the lower temperature. The deviation of the slope calculated for methanol at 10^{21} electrons cm^{-3} is about 25%; this is an order of magnitude larger and opposite in sign to that predicted from eq VII and the possible change of W indicated in Figure 2. However, good adherence to the relationship predicted for the absence of complications is observed at 200° and at electron densities less than 5×10^{20} electrons cm^{-3} , and we conclude that in this range intercept currents can be associated with complete collection.

Discussion

1. *Pressure Dependence of W and Autoionization.* At electron densities greater than 5×10^{20} electrons cm^{-3} there is a substantial decrease in intercept ion currents N_{ix}/N_{in} (Figure 2). At the same time, these intercepts are

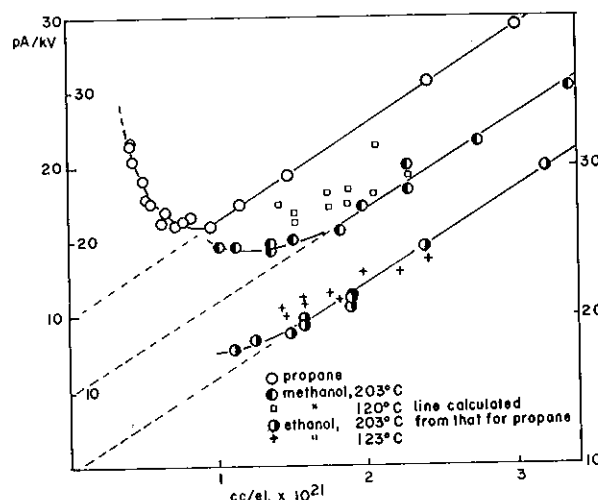


Figure 3. Variation of slope of ion current vs. collection potential plots with reciprocal electron density. Lines for methanol and ethanol are those calculated using the empirical constants derived from propane and correction for the difference in W . Scales are shifted vertically for clarity of presentation: top, propane; center, methanol, squares at 118° , circles at 204° ; bottom, ethanol, crosses at 123° , circles at 203° .

decreased by increases in slope which become density dependent in this range. Equation VII shows that this slope depends most strongly on density as a result of those terms which arise from incomplete collection. At equivalent electron densities, the behavior of different compounds will primarily depend on ionic mobilities. Since mobilities of all ions in strongly polar gases are much smaller than in hydrocarbons, the earlier onset of deviations from the predicted relationship for alcohols is qualitatively consistent with expectations.

The small change in N_{ix}/N_{in} in methanol at 200° at electron densities less than $5 \times 10^{20} \text{ cm}^{-3}$ (1.1%) is outside experimental error but it is possible that it is still a result of the same effects. At the same time it must be noted that in this density range the correction for incomplete stopping of the β particle becomes significant (ca. 1%).¹⁵ We believe, therefore, that the variation with ρ of extrapolated ionization currents in this range is still a result of incomplete ion collection.

The present measurements have not afforded the precision or reliability necessary to demonstrate unambiguously whether a mechanism such as that suggested in eq 1-4 significantly affects total ionization in alcohol vapors. The small change (ca. 1%) in N_{ix}/N_{in} for methanol may be taken as an upper limit for such a contribution. Extension of measurements to higher pressures using different source geometries to improve collection will be required and construction of a cylindrically symmetrical chamber for this purpose has been initiated.

2. *W Values for Alcohols.* The apparent difficulty in achieving complete ion collection may be a contributor to the divergence of W values for alcohols reported previously.²⁰⁻²² In the present study, W values can be obtained from the initial essentially pressure independent

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- (19) A. M. Howatson, "An Introduction to Gas Discharges," Pergamon Press, London, 1965, Chapter 3, p 53.
- (20) P. Adler and H. K. Bothe, *Z. Naturforsch.*, **20a**, 1700 (1965).
- (21) M. LeBlanc and J. A. Herman, *J. Chim. Phys.*, **21**, 1055 (1966).
- (22) R. Cooper and R. M. Mooring, *Aust. J. Chem.*, **21**, 2517 (1968).

TABLE I

Compound	W(alcohol), eV per ion pair					W(alkane) ^d
	a	b	c	This investigation		
				Temp, °C	W	
H ₂ O ^e	29.9	29.9	29.8	240	29.15 ± 0.09 ^e	28.8 ^f
CH ₃ OH	25.5	23.6	26.2	204	25.02 ± 0.09	26.94
C ₂ H ₅ OH	25.1	...	22.9	203	24.50 ± 0.09	24.18
<i>n</i> -C ₃ H ₇ OH	24.5	236	23.86 ± 0.08	23.96
<i>i</i> -C ₃ H ₇ OH	24.2	193	24.25 ± 0.09	23.96
<i>n</i> -C ₄ H ₉ OH	24.1	213	23.53 ± 0.12	23.16
CH ₃ CHOHC ₂ H ₅	201	23.53 ± 0.12	23.16
(CH ₃) ₂ CHCH ₂ OH	23.9	213	23.38 ± 0.11	23.50

^a P. Adler and H. K. Bothe, *Z. Naturforsch.*, 20a, 1700 (1965). ^b Water: C. Wingate, W. Gross, and G. Failla, *Radiat. Res.*, 8, 411 (1958); methanol: M. LeBlanc and J. A. Herman, *J. Chim. Phys.*, 21, 1055 (1966). ^c R. Cooper and R. M. Mooring, *Aust. J. Chem.*, 21, 2417 (1968). ^d T. A. Stoneham, D. R. Ethridge, and G. G. Meisels, *J. Chem. Phys.*, 54, 4054 (1971). ^e Errors are maximum deviations from the mean for water and the butanols and estimated for other compounds. ^f This value is for hydrogen and was taken from J. M. White, *Radiat. Res.*, 18, 265 (1963).

region of Figure 2 relative to $W(\text{N}_2) = 34.6$ eV/ion pair.²³ For methanol, ethanol, 1- and 2-propanol, the values cited correspond to the experimental measurements at the lowest electron densities shown in Figure 2, and the error limit given corresponds to the maximum deviation from the smooth curve drawn through the 200° data. For water and the butanols, W was obtained by averaging all data below an electron density of 7×10^{20} cm⁻³; the error given corresponds to the maximum deviation from this average and is therefore quite conservative. Also shown in Table I are W values reported by other investigators and the average energy required for ion pair formation in the corresponding alkanes.

Comparison with the earlier data of Adler and Bothe²⁰ shows our work to yield consistently lower W values; this may be ascribed to the uncertainties in the correction for back-scattering employed by these investigators, as well as to the possibility of incomplete collection; similarly, our $W(\text{H}_2\text{O})$ is the smallest reported. The low value reported for methanol by LeBlanc and Herman²¹ and that given for ethanol by Cooper and Mooring²² were both obtained by cavity ionization techniques using ⁶⁰Co γ rays, where energy deposition must be calculated from Bragg-Gray theory and errors may result when direct radiation interaction with the target gas takes place.

Within the homologous series, W decreases with increasing carbon number but is only little affected by the position of the hydroxyl groups; the three butanols investigated have W values within experimental error of each

other. Surprisingly, the change in W brought about by the substitution of a hydroxyl group for a hydrogen atom does not have a consistent effect on W . The tendency is to increase W but the reverse is observed for methanol, 1-propanol, and 2-methyl-1-propanol, although the last two have W values equal to their hydrocarbon counterparts within experimental error.

Conclusions

Experimental evaluations of W for alcohols are subject to error resulting from incomplete ion collection which does not manifest itself in deviations from linearity of the dependence of ion current on collection potential. With appropriate precautions it is possible to assess average energies required for ion pair formation at low pressures with an uncertainty which does not exceed 0.5%. Present data suggest that the contribution of autoionizing states with lifetimes greater than about 10^{-10} sec cannot exceed 1% of total ionization in methanol.

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