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.

LAFAYETTE, INDIANA

[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).

Deuterium, supplied by the Stuart Oxygen Company, was 99.5% pure. Acetylene and C_2D_2 were made by the reaction of pure water and D_2O, respectively, with a thoroughly calcined, high grade calcium carbide supplied by Electrometallurgical Company. Their isotopic purity was >99%. The C_2D_4 used was prepared by the method of Wilson and Wylie.[8] It was only 70% pure, the rest being C_2D_6 and C_2D_5H, but it was adequate for our purpose.

2.2. **Equipment and Technique.**—Except for the design of the electrodes, the equipment and technique used in this work on electric discharge through gas at atmospheric pressure was like that of Wiener and Burton.[5] Our electrodes were of nickel and fixed in position. The cathode was slightly concave at the point and protruded into a hole in the anode through which all the gas was forced. The discharge struck between the concave conical tip of the cathode and points along the circumference of the 3-mm. diameter hole in the anode. Thus, unlike the previous work,[5] interelectrode distance and disposition were fixed. Discharge was started with a Tesla coil. The current and voltage were controlled fairly reproducibly with a variable resistance in series in the circuit. The dead space of the discharge chamber was 3.3 cc. Since the starting volume of gas was uniformly 23.3 cc., 20 cc. was forced through the discharge region in each run.

The tar formed in each run was removed by wetting with dioxane and scraping with a thin brush of metal bristles inserted into the hole in the anode from the bottom.

2.3. **Analyses.**—Product samples from all runs were analyzed with a Consolidated analytical model (type 21-103A) mass spectrometer. Standard fragmentation patterns for deuterated ethylenes and acetylenes determined by Mohler, *et al.*, with a similar instrument[9] were found satisfactory for our use.

3. Results

3.1. **Ethylene.**—In a typical run about 0.8 mmole of C_2H_4 at atmospheric pressure was passed through the discharge at room temperature and 0.100 mmole was decomposed; the nature and amounts of the gaseous products in that case in mmole are

Hydrogen	0.126
Acetylene	.046
Methane	.0012
Butadiyne	.0037
Vinylacetylene	.00043
Benzene	.00016

Polymer was always produced; in this run, by material balance, its composition was $C_{3.6}H$. Such estimated composition of polymer varied considerably from run to run.

Table I summarizes the principal data obtained in the electric discharge runs with pure ethylene. Since a constant volume of gas at room temperature and atmospheric pressure was employed in all runs, the quantities of gas, all expressed in mmoles, are also approximately representative of the actual concentrations.

The kinetic treatment of these results is necessarily simplified. In a convenient model, the gas is visualized as a stream passing between two planar electrodes (not quite parallel to each other) between which a cylindrical electric discharge is passing. The instantaneous diameter of the discharge is roughly proportional to the square root of the current and its length is related to the voltage. The residence time, τ, in the discharge can only be very roughly estimated from the reciprocal flow rate t (*cf.* Table I). The discharge volume is of the order of 1 cubic mm.; thus, $\tau \simeq ct \simeq 10^{-3}\ t/20$. With t in the range of 1–2 sec., it follows that $\tau \sim 10^{-4}$ sec. This estimate involves the assumption (*cf.* section 4.2 b) that practically all the gas passes through the discharge region.

TABLE I

KINETIC DATA FOR PURE ETHYLENE[a]

Current, I, ma.	V, v.	t, sec./cc.	C_2H_4		C_2H_2	H_2	$-C_2/\Delta C_2H_4$	G-$(-C_2H_4)$[b]
			Initial	Final				
14	200	0.49	0.807	0.781	0.010	0.024	0.62	9.1
16	210	1.05	.801	.759	.025	.065	.40	5.9
16	180	1.94	.723	.654	.035	.090	.50	6.7
20	160	1.49	.806	.747	.028	.083	.54	6.0
30	130	0.50	.791	.770	.009	.033	.54	5.1
33	130	1.05	.829	.773	.025	.093	.56	5.8
30	130	1.10	.800	.750	.021	.075	.57	5.7
30	120	1.50	.800	.740	.026	.095	.57	5.4
32	140	2.10	.799	.719	.034	.125	.57	4.1
40	150	0.50	.799	.767	.016	.060	.50	5.2
40	150	1.05	.790	.732	.027	.097	.53	4.5
40	130	1.40	.795	.728	.032	.097	.52	4.5
40	150	2.10	.791	.681	.054	.153	.51	4.3
52	120	1.39	.805	.729	.032	.131	.58	4.2
60	120	0.60	.782	.750	.012	.054	.62	3.7
60	110	0.90	.786	.724	.024	.090	.62	5.1
58	120	1.55	.786	.688	.034	.159	.65	4.5
58	150	2.00	.794	.668	.051	.196	.59	3.5
58	125	2.53	.790	.649	.055	.211	.61	3.8
64	110	1.50	.801	.712	.035	.150	.61	4.1

[a] All composition data are given in millimoles. The initial values are for mmoles per 20 cc. The total volume of gas increases 5–10% during the runs. [b] G is calculated from the relationship $G = 4.82 \times 10^5\ \Delta/VIt$, where Δ is the particular change investigated in millimoles, and I is in milliamperes. In five additional runs in which t was adjusted to *ca.* 0.17 sec./cc. there was no systematic change in G.

For a rate of decomposition first order in ethylene, plot of log E_0/E_f (where E_0 and E_f refer, respectively, to initial and final concentrations of ethylene) against Vt (where V is the voltage of the discharge) at approximately constant current I should give a straight line.[5,10] Figure 1 shows such plots; within the limits of error of work of this kind the first-order law appears to be followed.

It can be shown from the argument of Wiener and Burton[5] that, since $\tau \simeq ct$

$$\frac{1}{Vt} \log \frac{E_0}{E_f} = \kappa_c I^n \qquad (1)$$

where κ_c and n are constants of the rate equation given by

$$\frac{dE}{d\tau} \simeq \frac{1}{c}\frac{dE}{dt} \qquad (2)$$

and

$$\frac{dE}{dt} \simeq -\kappa_c E V I^n \qquad (3)$$

The log-log plot[10a] of Fig. 2 suggests from the value

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(8) C. L. Wilson and A. W. Wylie, THIS JOURNAL, **75**, 5815 (1953).

(9) V. H. Dibeler, F. L. Mohler and M. de Hemptinne, *J. Research Natl. Bur. Standards*, **53**, 107 (1954); F. L. Mohler, V. H. Dibeler, L. Williamson and H. Dean, *ibid.*, **48**, 188 (1952).

(10) A typographical error on the ordinates in the Wiener–Burton paper makes some confusion. The units of Vt are volt sec./cc.

(10a) The proper value of E_f to be used in such plots is not really known. Actually, ratios of the initial and final *amounts* of ethylene are used. The resultant error (of about 5%) introduces a small error into the value of the logarithm.

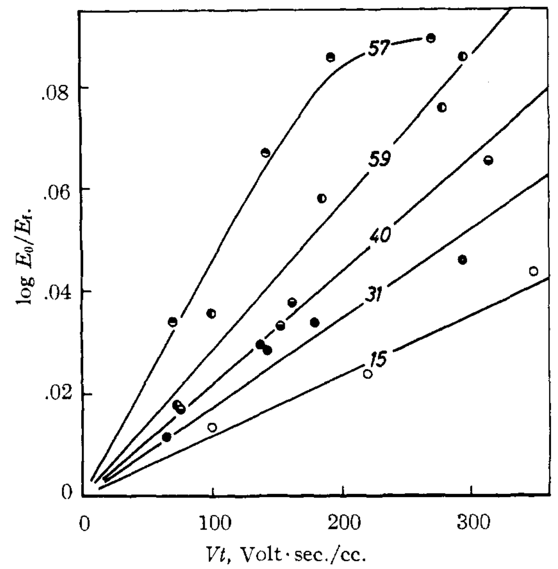

Fig. 1.—Decomposition of ethylene as affected by voltage and reciprocal flow rate at various currents (expressed in milliamp.). Data for samples which contained 10% H_2 are indicated by the symbol ◓.

of the slope that $n \sim 0.6$; *i.e.*, not far from 0.5. Since

$$G(-C_2H_4) = \frac{k}{VI} \times \frac{E_0 - E_t}{t} \qquad (4)$$

it follows that

$$G(-C_2H_4) \times I^{(1-n)}/E_{av} \sim k\kappa_e \qquad (5)$$

If the value 0.5 is adopted for n, the data of Table I yield $k\kappa_e = 3.92 \pm 0.36$ in arbitrary units, a reasonable degree of constancy for work and approximations of this kind.

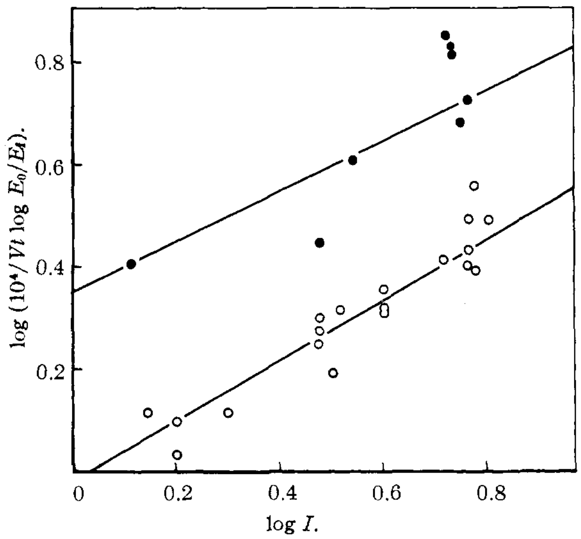

Fig. 2.—"Rate constant" as a function of current: ○, pure C_2H_4; ●, $C_2H_4 + D_2$.

3.2. Ethylene–Hydrogen Mixture.—One of the more striking aspects of addition of hydrogen is the reduction of carbon production and the increased fraction of ethylene going to acetylene; Fig. 3 shows that when hydrogen (or deuterium) comprises 75% of the total gas going through the discharge no carbon is produced and virtually the only carbon product is acetylene. Table II summarizes the data on effect of hydrogen. Figure 1 includes a curve constructed from the data of Table II for samples containing 10% hydrogen; in this case the average current is 57 ma. and there is a clear indication that the rate of decomposition of C_2H_4 (and production of C_2H_2 and H_2) increases on dilution with hydrogen. The data are not sufficiently extensive to indicate a departure from first-order dependence on ethylene concentration. The limited data are too widely scattered to permit determination of the nature of the dependence on hydrogen concentration.

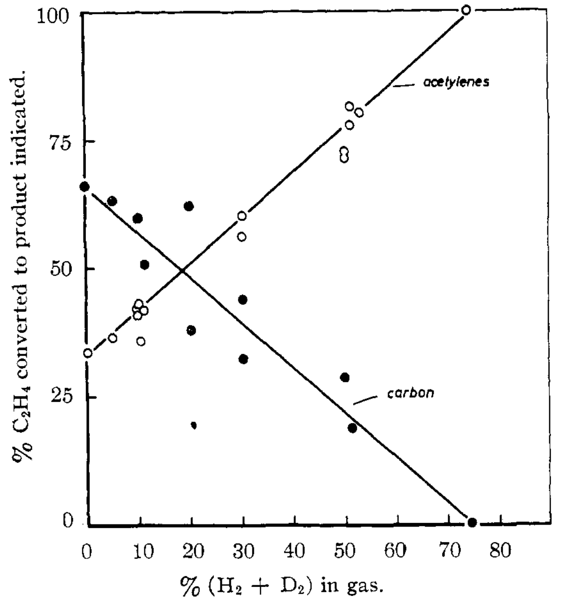

Fig. 3.—Effect of hydrogen and deuterium on efficiency of conversion of ethylene to acetylene.

3.3. Ethylene–Deuterium–Hydrogen.—Table III summarizes results of runs on various mixtures of ethylene and deuterium, with and without added hydrogen, at various currents and flow rates. As in the case of ethylene–hydrogen mixtures, the rate clearly increases with dilution of the ethylene.

In sections 3.1 and 3.2, E_t in equation *1* is unambiguously described since only hydrogen compounds are produced and any C_2H_4 formed by some back or exchange reaction cannot be recognized. When D_2 is present in the mixture, compounds like C_2H_3D, etc., also represent a loss of C_2H_4. However, only total decomposition is of interest in these kinetics. Consequently, E_t as employed in equation *1* is the sum of all residual ethylenes regardless of their isotopic composition and $\kappa_e I^n$ in Table III is calculated on that basis. In this work all reactions were conducted near atmospheric pressure. Thus, initial ethylene concentrations could not be varied without simultaneous variation of initial composition. However, at the current levels (*cf.* runs 69–72 and 73, 75, 76, 77 in Table III as well as some runs from Table II) for which initial compositions were fixed but E_0/E_t was varied, the values of $\kappa_e I^n$ are in sufficient agreement within the groups to indicate that rate re-

TABLE II

KINETIC DATA FOR MIXTURES OF ETHYLENE AND HYDROGEN

Current, I, ma.	V, v.	t, sec./cc.	H_2 Initial	C_2H_4		C_2H_2	H_2 Increase	CH_4	$G(-C_2H_4)$	$\kappa_e I^n \times 10^4$
				Initial	Final					
56	110	1.48	0.036	0.691	0.560	0.048	0.194	0.003	6.8	5.6
56	130	1.49	.078	.713	.586	.052	.182	.003	5.7	4.4
58	180	1.45	.158	.631	.500	.050	.174	.003	4.2	3.9
56	115	1.45	.240	.549	.454	.053	.120	.003	4.9	4.5
60	140	1.02	.079	.714	.612	.044	.150	[a]	5.6	4.7
56	140	0.50	.080	.714	.661	.019	.080	[a]	6.6	4.9
56	140	1.95	.078	.718	.585	.056	.203	[a]	4.3	3.3

[a] Not measured.

TABLE III

KINETIC DATA FOR MIXTURES OF ETHYLENE, DEUTERIUM AND HYDROGEN

Run no.	Current, I, ma.	V, v.	t, sec./cc.	D_2 Initial	H_2 Initial	C_2H_4		C_2H_2	C_2HD	C_2D_2	ΔH_2	HD	$-\Delta D_2$	C_2H_3D	$C_2H_2D_2$	C_2HD_3	C_2D_4	$\kappa_e I^n \times 10^4$
						Initial	Final											
69	58	125	1.90	0.088	0	0.708	0.617	0.040	0.008	...	0.141	0.036	0.027	0.002				2.5
70	56	140	1.45	.088		.705	.621	.029	.006		.104	.029	.019	.002				2.7
71	58	130	1.00	.088		.707	.652	.020	.006		.070	.019	.014	.001				2.7
72	58	130	0.55	.087		.697	.632	.016	.006		.059	.018	.006	.001				5.9
74	56	220	1.50	.241		.555	.386	.060	.037	0.006	.176	.105	.083	.008	0.002	0.001	0.001	4.4
73	54	230	1.10	.394		.394	.251	.033	.043	.016	.122	.158	.131	.011	.004			6.7
75	53	250	1.50	.394		.394	.203	.032	.043	.018	.155	.194	.123	.008	.002			7.1
76	56	250	1.95	.399		.399	.216	.045	.054	.022	.170	.194	.157	.011	.005			4.8
77	54	250	0.50	.399		.399	.322	.017	.024	.009	.067	.095	.076	.007	.002			6.5
83	13	220	1.00	.408		.387	.334	.010	.014	.006	.051	.064	.058	.005	.002			2.5
84	30	240	1.05	.407		.387	.322	.013	.022	.011	.054	.090	.079	.005	.002			2.8
85	35	270	1.10	.408		.387	.277	.026	.036	.015	.096	.134	.118	.010	.004	.003	.001	4.0
86	58	250	1.10	.408		.387	.256	.031	.043	.016	.113	.162	.140	.012	.005	.003	.001	5.3
88	50	320	1.13	.291	0.323	.204	.133	.035	.024	.006	.046	.170	.123	.006	.002			4.3
89	54	260	1.10	.202	.218	.380	.274	.052	.023	.004	.095	.099	.080	.006	.002			4.5
92	53	230	1.10	.261	.092	.447	.380	.038	.018	.003	.067	.071	.105	.006	.002			2.7

mains first order in ethylene during runs; departures from good agreement probably represent experimental error. The added gas has such a large effect on $\kappa_e I^n$, according to a relation which does not appear first power in the diluent, that one might conclude that the formation of hydrogen in decomposition of ethylene must produce effects which certainly prevent exact adherence to the relationship expressed by equation *1*. Figure 2 shows a plot of log ($\kappa_e I^n$) against log I for the eight runs with approximately 50% deuterium. Within the wide scattering of the data, it appears that the "rate constant" remains roughly half order in the current.

In general, increase in t results in greater conversion to products irrespective of the current and voltage employed. Another rather obvious feature of the results is that, in the presence of large excess of deuterium, much of the hydrogen liberated from C_2H_4 by the discharge appears not as H_2 but as HD. At the same time, however, the samples do not become equilibrated with respect to H_2, HD and D_2.[11]

3.4. Ethylene–Acetylene Mixtures.—Table IV gives the results of some exploratory runs on the role of acetylene in the reaction. The latter in general tends to lower the operating voltage of the discharge. In Table IV $\kappa_e I^n$ has the same significance as in the previous section; $\kappa_a I^m$ refers to a relationship analogous to equation *1* involving, however, the acetylenes. Thus A_f is the sum of the final concentration of C_2D_2 and acetylenes derived therefrom. In the computation the assumption was made that C_2HD represented all the acetylenes formed by H-atom exchange with C_2D_2 or, effectively, that any C_2HD converted to C_2H_2 was approximately balanced by C_2HD formed from C_2H_2; since the total amount of C_2HD involved is very small, this approximation introduces no significant error. Log-log plots of $\kappa_e I^n$ and $\kappa_a I^m$ against I indicate, within the wide scattering of the limited data, that n may be approximately unity, while m is near 0.7. There is thus some question of the effect of C_2H_2 concentration on the half-order dependence on current.

The few data show that $\kappa_e I^n$ (*i.e.*, the "rate constant" for C_2H_4 disappearance) increases in presence of C_2H_2; the rate of the reaction, however, remains first order in C_2H_4. The information on the acetylene decomposition is less clear-cut; the conclusion of *ca.* 0.7 order dependence on I is based on the assumption that $\kappa_a I^m$ is properly defined by an equation analogous to 1. Actually, an assumption is made that $-dA/d\tau$ is linearly dependent on A and the few "constants" thereby derived are found *ca.* 0.7 order dependent on I; *i.e.*, the statements regarding dependence of C_2D_2 disappearance on both I and A are consistent with the data but not proven.

A point worthy of note is that in the C_2D_2 runs C_2D_2(initial)/C_2H_4(initial) $\simeq$ HD/H_2 $\simeq$ 0.2. Production of D_2 is almost negligible.

3.5. Ethylene–Ethylene-*d*$_4$.—The C_2D_4 available to us was considerably contaminated (*cf.* section 2.1) with C_2D_3H (*i.e.*, ~8%) and with

---

[11] The value of n_H = $(HD)^2/(H_2)(D_2)$ becomes K for complete equilibration *i.e.*, a quantity slightly less than 4, depending on the temperature. The experimental values are considerably less.

TABLE IV

KINETIC DATA FOR MIXTURES OF ETHYLENE AND ACETYLENE

I, ma.	59	59	54	56	40	31	19
V, volts	110	90	120	115	140	140	170
t, sec./cc.	1.10	1.05	1.00	1.04	1.05	1.05	1.06
C_2H_4 initial	0.752	0.702	0.611	0.667	0.670	0.668	0.661
C_2H_2 initial	.040	.078	.169				
C_2D_2 initial				.131	.132	.131	.130
C_2H_4 final	.669	.628	.542	.574	.599	.616	.610
C_2H_3D				.002	.003	.002	.002
C_2H_2 final	.064	.088	.153	.023	.020	.017	.015
C_2D_2 final				.112	.116	.118	.118
C_2HD				.008	.007	.005	.004
H_2	.144	.113	.101	.095	.068	.054	.037
HD				.019	.014	.011	.008
D_2				.001	.0007	.0008	small
$\kappa_e I^n \times 10^4$	4.2	5.1	4.3	5.3	3.2	2.3	1.8
$\kappa_e I^n \times 10^4$ (in pure C_2H_4)	2.9	2.9	2.6	2.7	2.1	1.9	1.4
$\kappa_a I^m \times 10^4$				3.4	2.2	2.1	1.5

mixed ethanes ($\sim$30%). Single experiments with such C_2D_4 and a 50–50 C_2H_4–C_2D_4 mixture gave the expected range of products. A particularly noteworthy point in the latter experiment is that the H_2–HD–D_2 product ratio indicated practically complete equilibration of the hydrogen[11]; *i.e.*, n_H = 3.9 in this case. This result is quite different from that for C_2H_4–D_2 mixtures (section 3.3) where n_H never exceeded 0.9.

3.6. Electron-energy Effects.—The average energy of an electron in glow-type electric discharge is usually of the order of a few electron-volts or less, whether the discharge occurs at atmospheric or low pressure. On the other hand, in radiation chemistry a significant fraction of the primary effects is caused by electrons with an energy of the order of 10^5 e.v. Table V shows that differences in the energies of the incident electrons, as well as of the pressure, cause significant differences in nature and amounts of products formed from ethylene.[12]

TABLE V

EFFECT OF IMPINGENT ELECTRON ENERGY AND OF PRESSURE ON PRODUCTS FROM ETHYLENE DECOMPOSITION (ANALYSIS IS EXPRESSED IN MOLE %)

Energy source	Glow discharge		Van de Graaff
Electron energy	Low		1.5 Mev. (initial)[a]
Pressure, mm.	750	10	750
H_2	71%	73.1%	14.4%
C_2H_2	25.9	8	29.5
C_2H_6		4.3	29.1
CH_4	0.7	6.5	1.0
C_4H_2	2.1		0.04
C_4H_4	0.24		0.24
C_4H_6			0.09
C_3H_6		1.8	2.4
C_3H_4			0.35
C_3H_8		2.9	13.6
C_4H_{10}		2.1	6.6
C_4H_8		1.3	2.3
C_6H_6	0.10		

[a] Other products from decomposition of ethylene by 1.5 Mev. electrons include C_5H_{10}, C_5H_{12}, C_6H_{12}, C_6H_{14} and C_8H_{18}, all to the extent of *ca.* 0.1% or less.

4. Discussion

4.1. Character of the Discharge.—The atmospheric pressure electric discharge with cooled cathode has been discussed at some length by Wiener and Burton.[5] For the purpose of the present paper, there appears little to add to their description here. Essentially, this type of discharge is merely a condensed glow with the positive column extending nearly all the distance between the electrodes. It is found in unconstrained glow discharges at low pressure that at low current only a small fraction of the electrode area is covered by the discharge. When an effort is made to increase the voltage, the current increases instead but the current density, as observed at the electrode, remains fairly constant. The cross-sectional area of the discharge is nearly proportional to the current.[13] If an atmospheric discharge, such as employed in this work, retains these characteristics of an unconstrained discharge, it follows that the instantaneous diameter of the discharge region is approximately proportional to $I^{1/2}$.

The discharge column does not oscillate much. It shifts position every 2 or 3 seconds and sometimes gets stuck in one position for as long as 10 sec. During the time $\tau \sim 10^{-4}$ sec. required for a "piece" of gas to pass through the discharge, the latter consequently is substantially at rest. The results here reported (*cf.* section 3.3) clearly show that increase in t results in greater conversion to products irrespective of current and voltage employed. A reasonable view of the facts is that the gas actually pursues a swirling course between the electrodes so that a single piece of gas is almost certain to pass through the discharge column at least once. The residence time τ is then proportional to the distance the gas must travel *across* the discharge column and is given by

$$\tau \simeq c'tI^{1/2} \qquad (6)$$

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(12) In the radiation chemistry work the technique of exposure was essentially that described by J. P. Manion and M. Burton, *J. Phys. Chem.*, **56**, 560 (1952). In the low pressure glow discharge work the technique was similar to that of J. C. Devins and M. Burton, THIS JOURNAL, **76**, 2618 (1954).

(13) For extensive discussion of the glow discharge and its various details, *cf.* L. B. Loeb, "Fundamental Processes of Electrical Discharge in Gases," John Wiley and Sons, Inc., New York, N. Y., 1939, chapter XI; especially p. 563. For a discussion of the details of the high pressure glow discharge, *cf.* J. M. Meek and J. D. Craggs, "Electrical Breakdown of Gases," Oxford University Press, London, 1953, p. 448.

and

$$\frac{dE}{d\tau} \simeq \frac{1}{c'I^{1/2}}\frac{dE}{dt} \qquad (2')$$

The corresponding rate expression

$$\frac{dE}{dt} = -\kappa_e EVI^{\sim 1/2} \qquad (3')$$

has the same form as *3* but the value $n \sim 1/2$ appears without kinetic significance. This view makes the value of n essentially an artifact resultant from the way gas flows through the discharge region. Should it always flow directly transverse to the discharge, n would closely approximate $1/2$. However, if a variation of current is accompanied by a corresponding variation in the angle at which the gas passes through the discharge, n could be made to vary considerably from $1/2$.

4.2. Some Interpretations of the Data. a.—The data clearly show that increase in t results in greater conversion to products according to a simple law, irrespective of current and voltage employed. Since t is representative of τ, the residence time in the discharge, the conclusion is that the chemical reaction occurs to a significant extent only in the discharge region itself. Since τ is of the order of 10^{-4} sec., reaction is substantially complete in that time.

b.—The simple law relating E_0/E_t to t shows that, in the sample of gas in the discharge region, uniform conditions prevail throughout the time τ, *i.e.*, that effectively the entire sample is subjected to discharge conditions in a uniform way throughout the entire residence time. This fact is pointed up by those experiments (*cf.* run 75 in Table III) in which the simple kinetic law is followed up to almost 50% decomposition.

c.—In most cases disappearance of C_2H_4 is $\sim 1/2$ order in I (*cf.* sections 3.1, 3.3 and 4.1). Possible first-order dependence on I in presence of C_2H_2 requires more extensive data both for confirmation and for interpretation.

d.—Decomposition rates of ethylene and acetylene appear first order in those compounds (*cf.* sections 3.1 and 3.4). The latter point is, however, not definitely proven.

e.—In presence of a large excess of D_2 (*cf.* Table III and section 3.3), much of the hydrogen liberated from C_2H_4 by the discharge appears as HD (not as H_2); however, the samples do not become equilibrated with respect to H_2, HD and D_2. These facts show that, if H atom is involved, the reaction

$$H + D_2 \longrightarrow HD + D \qquad (12)$$

competes effectively with

$$H + C_2H_4 \longrightarrow H_2 + C_2H_3 \qquad (8)$$

but that reaction 12 and its counterpart

$$D + H_2 \longrightarrow HD + H \qquad (12')$$

is not so rapid as to permit equilibration of the hydrogens in the time available for reaction in the discharge. On the other hand, the H_2–HD–D_2 mixture produced by the discharge through the C_2H_4–C_2D_4 mixture is equilibrated (*cf.* section 3.5). These two results taken together mean simply that in the later case neither H_2 (nor D_2) can be formed in a single step by rearrangement decomposition of ethylene but that acetylene is formed only stepwise from it.[14] Wiener and Burton[5] have expressed a similar conclusion regarding the mechanism of decomposition of methane.

Another point worthy of note is that in the experiments in which C_2H_4 was decomposed in the presence of D_2 at large concentration, the amount of C_2H_3D produced was always small relative to the amount of C_2H_4 decomposed. Since, according to the conclusions of the preceding paragraph, C_2H_3 is an intermediate in the formation of acetylene, it follows that the reaction

$$C_2H_3 + H_2 \longrightarrow C_2H_4 + H \qquad (13)$$

plays a minor role as a back reaction in those cases in which H_2 was not initially added and can be neglected (to a satisfactory approximation) in a consideration of the detailed mechanism.

f.—In the runs in mixtures of C_2D_2 and C_2H_4 (*cf.* section 3.4 and Table IV) HD and H_2 are produced in ratio approximately equal to the ratio of initial concentrations of C_2D_2 and C_2H_4 but production of D_2 is almost negligible. This result means that (i) C_2D_2 does *not* decompose by rearrangement decomposition in the discharge to yield C_2 and D_2 in a single act, (ii) if H atoms are involved, the specific rates of the reactions

$$H + C_2D_2 \longrightarrow HD + C_2D \qquad (14)$$

and 8 are approximately equal at the temperature of the discharge, and (iii) C_2D_2 does not decompose to a significant extent by any process which yields atomic D (otherwise, a reaction analogous to 14 would become important and D_2 would be produced). Since reactions 14 and 8 should have steric factors of the same order of magnitude, a conclusion corollary to ii is that, if they are responsible for H_2 and HD production, their activation energies *for the H atoms involved* (it must not be forgotten that the atoms may be "hot") are approximately equal. An alternative view, which detailed examination of the kinetics eventually evoked, is that reactions 8 and 14 are most probably not the source of H_2 and HD.

g.—Rate of reaction appears always to be first order in voltage. Initial admixture of C_2H_2 (or C_2D_2) appears to lower operating voltage of the discharge (*cf.* section 3.4) and initial admixture of H_2 (or D_2) increases the required operating voltage considerably (*cf.* particularly Table III). Hydrogen (or deuterium), by its presence, increases C_2H_2 yield, decreases carbon production and increases the rate of the reaction.

h.—The products from decomposition of ethylene induced by high-energy electrons are determined by pressure as well as by energy of the electrons. This point is further elaborated in section 4.6.

4.3 Electron-energy Considerations.—The approximate formula[5,15] for the average energy E_{av} of the electrons in a field of potential gradient X is

$$E_{av} = eX\lambda/2\alpha^{1/2} \qquad (7)$$

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(14) The simultaneous removal of two H atoms as such requires *ca.* 6.2 e.v. compared with a minimum of *ca.* 4 e.v. for reaction 2. Since a major problem is to account for availability of energy even so low as 4 e.v., the possible contribution of such a one-step reaction as $C_2H_4^* \rightarrow C_2H_2 + 2H$ is not considered.

(15) *Cf.* K. K. Darrow, "Electrical Phenomena in Gases," Williams and Wilkins, Baltimore, Md., 1932, p. 177.

where λ, the mean free path of the electron, is dependent mainly on the pressure and α, the average fractional energy loss by the electron on collision with a molecule, is dependent on the energy of the electron and the nature of the gas. According to Massey and Burhop[16a] the cross-section for elastic collision for 1 volt electrons in C_2H_4 or C_2H_2 is *ca.* 14 Å.^{2}. The corresponding mean free path at 760 mm. pressure even at 1000° (far in excess of the estimated temperature of the discharge[5,17]) is $\ngtr 1.2 \times 10^{-4}$ cm. The quantity α is not known for C_2H_4 but a lower limit of 0.02 may be assumed on the basis of values for NH_3 and CO_2.[16b] In the atmospheric pressure work X was about 1000 volts per cm. so that E_{av} calculates to be *ca.* 0.5 e.v. at a maximum. The product $X\lambda$ tends to remain constant with variation in pressure so that E_{av} has about the same value in the low pressure experiments (*cf.* Table V).

This method of estimation of E_{av} is considerably over-simplified. The quantity α is sensitive to the actual energy of the electron and may rise to high values whenever resonance transfer of energy occurs; it may be expected that the cross-section for energy transfer is also high under such conditions. Both of these factors tend to reduce E_{av} and certainly to lower the upper limit of the electron-energy range. The immediately resultant question concerns the manner in which the molecules can be raised to energies sufficient for bond breakage (about 4 e.v.) by electrons whose maximum effective energy is probably $\ngtr 2$ e.v. This problem has been considered by Burton and Magee[18] who suggested a mechanism of successive excitation in which a molecule or free radical is raised through a series of optically forbidden transitions to an energy level at which it decomposes or transfers its energy to a species which can decompose. For the case of methane,[7] they suggested the free radical CH_2 as the species by which the electron energy was transferred into the gas. In this case (*cf.* section 4.5), C_2H_3 can be assumed to play an analogous role but the evidence is not clear and it is more convenient not to specify the species involved. As a matter of fact the effect of acetylene on the operating voltage of the discharge (section 4.2 **g**) suggests that it may play the role.

4.4. The Role of Hydrogen.—The potential gradient required for operation of the discharge through ethylene is increased by initial admixture of H_2. Correspondingly (*cf.* equation 7), E_{av} is increased. In the present state of our knowledge the kinetic consequences of this effect cannot be assessed.

The role of H_2 in increasing C_2H_2 yield and in decreasing free carbon production is best seen by reference to Table III. When D_2 is added in large amount, C_2HD and C_2D_2 are both formed to significant extent. The implication is that the reaction

$$C_2H + D_2 \longrightarrow C_2HD + D \qquad (7')$$

is important and that H_2 is important in increasing C_2H_2 yield and decreasing carbon production mainly because it enters into a reaction analogous to 7′ before the C_2H can be decomposed in a second step to carbon. This view is consistent with the conclusion of section 4.2 **f** that formation of carbon from C_2H_2 must involve a two-step process in which C_2H is an intermediate.

4.5. Mechanism.—The special requirements of a mechanism of the decomposition of C_2H_4 to C_2H_2 are indicated in sections 4.1–4.4. A minimum set of reactions which must be included appears to be

$$C_2H_4 \rightsquigarrow C_2H_4^* \qquad (1)$$

$$C_2H_4^* \longrightarrow C_2H_3 + H \qquad (2)$$

$$\mathbf{S} \rightsquigarrow \mathbf{S}' \dashrightarrow \mathbf{S}'' \qquad (3)$$

$$\mathbf{S}' + C_2H_3 \longrightarrow \mathbf{S} + C_2H_3' \qquad (4)$$

Reaction 1 is significant only in the initiation of the discharge. According to the concept of the role of a successive excitation mechanism,[7] reaction 1 does not occur in an existent discharge. Reaction 2 is the "chain initiator" in such case. The species **S** which is excited in reaction 3 by a succession of optically forbidden processes to **S**′ and **S**″ successively is probably the free radical C_2H_3 but may also be C_2H_2 or even C_2H. Thus, step 4 may have only formal significance; it is important that an excited vinyl radical appears to play a role.

In regard to subsequent reactions, a number of mechanisms have been tested including particularly those which involve decomposition of C_2H_3' to C_2H_2 and H. However, the only one found consistent with most of the data and thermochemical requirements involves Stern–Volmer reactions of C_2H_3'

$$C_2H_3' + C_2H_4 \longrightarrow C_2H_2 + C_2H_3 + H_2 \qquad (5)$$

$$C_2H_3' + C_2H_2 \longrightarrow C_2H_2 + C_2H + H_2 \qquad (6)$$

$$C_2H + H_2 \longrightarrow C_2H_2 + H \qquad (7)$$

$$H + C_2H_4 \longrightarrow H_2 + C_2H_3 \qquad (8)$$

$$\mathbf{S}'' + C_2H_4 \longrightarrow \mathbf{S} + C_2H_4^* \qquad (9)$$

$$2C_2H \longrightarrow \text{Chain termination} \qquad (10)$$

In reactions 5 and 6, both reactants are presumed to contribute H atoms to the H_2 molecule. A hydrogen extraction reaction between H and C_2H_2 (*cf.* reaction 14), is explicitly omitted; speculations regarding other paths of destruction of C_2H_2 are not warranted by the data.[19]

Steady-state treatment of the total mechanism yields the equations

$$\frac{dE}{d\tau} = - r_3' \frac{k_5E}{k_5E + k_6A'} - k_7 \left(\frac{2k_2E^*}{k_{10}}\right)^{1/2} (H_2) \qquad (8)$$

For the disappearance of C_2D_2 in a mixture of C_2D_2 and C_2H_4, the following approximate relationship results

$$\frac{dA}{d\tau} \simeq - r_3' \frac{k_6A}{k_5E + k_6A} \qquad (9)$$

Although equations *8* and *9* are conventional rate expressions, the value of τ itself in the integrated expressions is a function of I; *i.e.*, $\tau \propto I^{1/2}$ (*cf.* section 4.1) and reduces to zero when I is zero.

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[16] H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, New York, N. Y., 1952, (a) p. 208; (b) p. 279.

[17] J. Chanmugam and M. Burton, THIS JOURNAL, **78**, 509 (1956).

[18] M. Burton and J. L. Magee, *J. Chem. Phys.*, **23**, 2194 (1955).

[19] We are indebted to the referee for the comment that the mechanism as given does not of itself account for HD production in presence of excess D_2. A suggestion consistent with our conclusions is that while reactions like 12 and 12′ (ensuant on reaction 7) do not give equilibration of H_2 and D_2 in the time available, they as well as the reaction $D + C_2H_4 \rightarrow HD + C_2H_3$, occur at a sufficient rate to give a significant yield of HD.

Because its current density is approximately constant and independent of current, it is presumably in the character of an unconstrained glow discharge column that its properties (apart from those near the exterior surface) are unaffected by its diameter; *i.e.*, by the current. Thus, in the discharge column itself, in the steady state the concentrations of intermediates (*e.g.*, E^*) are approximately independent of current; a particular rate like r_3' is likewise independent of the current. These statements are essentially equivalent to the statement that apart from surface effects, the steady-state conditions are not affected by the volume of the reactant system.

Expression *8* indicates that $\mathrm{d}E/\mathrm{d}\tau$ can be (a) approximately first order in ethylene concentration E and independent of acetylene concentration if k_5 and k_6 are approximately equal, as is required by the considerations of section 4.2 **f**, (b) independent of I because r_3' and E^* are independent of I, (c) dependent on hydrogen concentration, and (d) depart from first-order dependence on E in presence of excess H_2 (*cf.* section 3.2). Since the effect of H_2 on the potential gradient as well as on r_3' is not shown, the form of the dependence on hydrogen concentration cannot be read from expression *8*.

In regard to conclusion *a* the approximate equality of k_5 and k_6 is not only an implicit requirement deriving from the ratio of H_2/HD yields in mixed C_2H_4 and C_2D_2 but also a direct requirement of the kinetic data when interpreted according to the scheme leading to expressions *8* and *9*. At low initial H_2 concentration, with C_2D_2 as the only acetylene compound present in significant quantity, equation *8* reduces to

$$\frac{\mathrm{d}E}{\mathrm{d}\tau} \simeq -r_3' \frac{k_5E}{k_5E + k_6A} \qquad (10)$$

analogous to equation *9*. However, from equations *2*, etc.

$$\left.\begin{aligned} \mathrm{d}E/\mathrm{d}\tau &= -\frac{1}{c}\kappa_e E\,VI^n \\ \mathrm{d}A/\mathrm{d}\tau &= -\frac{1}{c}\kappa_a A\,VI^m \end{aligned}\right\} \qquad (11)$$

Since Table IV indicates that $\kappa_e I^n \simeq \kappa_a I^m$

$$k_5 \simeq k_6 \qquad (12)$$

just as the analytical results seem to require.

The limited data of Table IV do not permit analysis of the acetylene kinetics. There is nothing in the scheme presented which would suggest that dependence of $\mathrm{d}E/\mathrm{d}\tau$ on I might be a function of acetylene concentration. A more elaborate study of the effect of C_2H_2 is required to establish the reality of such a phenomenon, to resolve the anomaly if it does exist, and to establish more precisely the role of acetylene in the decomposition of C_2H_4.

4.5.1. Yields.—The high G value of *ca.* 30 reported by Schoch[6] for the *over-all* reaction

$$C_2H_4 \longrightarrow \text{Products} \qquad (11)$$

is easily understood on the basis of the dominant role of reaction 5 in the suggested mechanism. The minimum energy of the species C_2H_3' required in reaction 5 is exactly the ΔH of reaction 11; *i.e.*, 42 kcal. Thus, any G value permitted by the thermochemical requirements of reaction 11 (*i.e.*, < 56) fits the proposed mechanism.

4.6. Products as Determined by Electron Energy and Pressure.—The average energy of the electrons in electric discharge is given by expression *7*. Factors such as more ready access to the walls at low pressure tend to deplete the free radical concentration and thus to change the composition of the gaseous medium as compared with the conditions of an atmospheric pressure discharge. Thus, there are resultant changes in the values of α. However, $X\lambda$ remains fairly constant and it may be concluded that both at low and atmospheric pressures the value of E_{av} is of the order of one or two electron volts. On the other hand, in radiation chemistry about one-quarter to one-third the effects are produced by high-energy electrons; the so-called low-energy electrons of such irradiation may have typical energies ranging up to 75 e.v. with only *ca.* $^1/_{15}$ the energy in that range being contributed by electrons of < 5 e.v. energy. Nevertheless, many of the yields of the low pressure discharge (*cf.* Table V) resemble those from Van de Graaff-electron irradiation more than those from the atmospheric pressure discharge.

The explanation of what superficially appears to be an anomaly in the results of Table V doubtless resides in differences in the fates of the intermediates at low and atmospheric pressure. On the other hand, lowered yield of H_2 accompanied by high yield of C_2H_2 and C_2H_6 in Van de Graaff-electron irradiation of C_2H_4 probably reflects the effects of the ionized and other highly excited species which are the important primary products of the bombardment.

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