

and 4, where the amino function partakes in salt formation, essentially linear behavior is obtained over the whole pH range. The lines have slopes varying from -0.04 to -0.07 . Though Hammett's equation is applicable for the polarographic reduction of quinoxalines to the *dihydro* stage, the influence of substituents is relatively weak. For example, Brockman and Pearson⁶ obtained slopes of -0.25 in their study of the polarographic reduction of benzophenones.

The variations in heights of the second major wave with pH are influenced by the electronic nature of the substituents. The electron-acceptor substituents, bromo and chloro, cause the heights to decrease with increasing pH whereas electron-donor substituents, ethoxy and methoxy, cause the heights to increase with increasing pH up to and

including pH 6. These trends can be explained qualitatively on the basis that catalytic activity increases with increasing dissociation of the 1,4-dihydroquinoxalinium ion. Electron-acceptor substituents cause the pK_a 's to be lower than for the electron-donor containing systems. In each instance the proton removed from the monobasic 1,4-dihydroquinoxalinium ion comes from N^1 , the "para" nitrogen.

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MADISON, NEW JERSEY

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Mass Spectra of Propyne and Propyne- d_3 , and the Appearance Potentials of $C_3H_4^+$, $C_3H_3^+$ and Equivalent Deuterated Ions

BY J. COLLIN¹ AND F. P. LOSSING

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A comparison of the mass spectra of CH_3CCH and CD_3CCH shows that extensive migration of hydrogen atoms occurs in the propyne ion, the loss of H and D atoms occurring on a statistical basis. The appearance potentials of the $C_3D_3^+$ and $C_3D_2H^+$ ions from CD_3CCH do not show the difference in the energy of formation which would be expected if these ions were CD_3CC^+ and $^+CD_2CCH$, respectively. It is concluded that the $C_3D_3^+$ and $C_3D_2H^+$ ions are both propargyl ions, and that their formation involves an extensive rearrangement of hydrogen atoms. From a consideration of the value of $D(H-C_3H_3)$ derived from these appearance potentials it is concluded that the excess energy available for the rearrangement is appreciably less than 9 kcal./mole, and is possibly almost zero. The ionization potentials of C_3D_2H and C_3H_4 are found to be the same within the experimental error.

Introduction

From a study of the appearance potentials of the $C_3H_3^+$ ion produced from allene, propyne, butyne and 1,2- and 1,3-butadienes by electron impact² it was concluded that this ion had the propargyl $^+(\text{CH}_2-\text{C}\equiv\text{CH})$ structure. It might therefore be expected that the formation of the $C_3H_3^+$ ion from propyne would be a simple process in which a H atom is split off from the methyl group, without any rearrangement of hydrogen atoms being involved. On the other hand, some preliminary experiments on the mass spectrum of $CD_3-\text{C}\equiv\text{CH}$ showed that, at least with 50 volt electrons, the loss of H and D was in the ratio 1:3, suggesting that in the $C_3H_4^+$ ion all the hydrogens were equivalent.³ Furthermore, the ionic heats of formation indicated that the formation of the $C_3H_3^+$ ion from 1,3-butadiene and 2-butyne, for which a migration of a hydrogen atom is necessary, proceeds with little or no activation energy. In view of this, it is of interest to find whether the apparently straight-forward process for formation of the $C_3H_3^+$ ion from propyne itself also involves a migration and, if so, whether the required activation energy is sufficient to invalidate the determination of $D(C_3H_3-H)$ in propyne.²

Consequently the abundance of C_3 ions and C_2 ions in the spectrum of propyne and of propyne- d_3 have been compared at lower electron energies, and the appearance potentials of $C_3D_3^+$ and $C_3D_2H^+$ ions have been measured and compared with the corresponding ion in propyne itself.

Experimental

The propyne was obtained from Farchan Research Laboratories. The sample of propyne- d_3 , prepared by Merck and Company (Canada) was found to be 97.7–98.0% $CD_3-\text{C}\equiv\text{CH}$, the remainder being mainly $C_3D_2H_2$. Corrections were made to the mass spectra to remove the small contributions from this impurity. The mass spectrometer was a 90° Nier-type, and the method of measuring the appearance potentials was the same as that used previously.²

Results and Discussion

The relative intensities of C_3 and C_2 peaks in the mass spectrum of propyne at different electron accelerating potentials are given in Table I. In Table IIa are shown the corresponding peak intensities for propyne- d_2 . In both cases the peaks have been corrected for contributions from carbon-13, and the propyne- d_3 spectrum has been corrected for contributions from the propyne- d_2 impurity. In Table IIb the spectrum of propyne- d_3 has been simplified by combining peaks of similar composition to facilitate comparison with the propyne spectrum. It can be seen that the intensities are quite similar for C_3 peaks but less so for C_2 peaks.

The most interesting feature of the spectrum in Table IIa is the ratio of the $C_3D_3^+$ and $C_3D_2H^+$

(1) National Research Council of Canada Postdoctorate Fellow 1956–1957. Institut de Chimie Générale, Université de Liège, 1B Quai Roosevelt, Liège, Belgium.

(2) J. Collin and F. P. Lossing, *THIS JOURNAL*, **79**, 5848 (1957).

(3) J. B. Farmer and F. P. Lossing, *Can. J. Chem.*, **33**, 861 (1955).

TABLE I
MASS SPECTRUM OF PROPYNE AS A FUNCTION OF ELECTRON ACCELERATING POTENTIAL^a

m/e	Ion	Electron accelerating potential (volts)												
		50	40	30	25	20	19	18	17	16	15	14	13	12
40	$C_3H_4^+$	37.40	39.20	42.77	40.85	61.54	64.42	68.01	71.26	75.43	80.97	87.92	94.89	98.05
39	$C_3H_3^+$	32.20	33.00	34.80	36.55	33.19	31.91	29.31	26.79	23.18	18.24	11.57	4.90	1.95
38	$C_3H_2^+$	12.58	13.03	13.21	10.99	4.01	2.88	2.06	1.41	1.08	0.73	0.50	0.17	...
37	C_3H^+	9.20	9.13	5.85	1.98	0.01
36	C_3^+	2.42	1.83	0.21	0.01
27	$C_2H_3^+$	0.25	0.28	.26	.14	.04	0.04	0.03	0.02
26	$C_2H_2^+$.98	1.03	.62	.31	.19	0.19	0.18	0.17	0.15
25	C_2H^+	.92	0.73	.23	.09
24	C_2^+	.37	0.15	.02

^a The abundances are expressed in percentages of the total ionization.

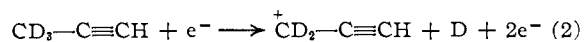
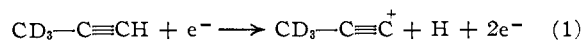
TABLE IIa
MASS SPECTRUM OF PROPYNE- d_3 AS A FUNCTION OF ELECTRON ACCELERATING POTENTIAL^a

m/e	Ion	Electron accelerating potential (volts)												
		50	40	30	25	20	19	18	17	16	15	14	13	12
43	$C_3D_3H^+$	38.81	40.23	45.45	49.71	63.21	65.94	67.88	73.40	78.14	82.62	88.15	95.60	98.47
42	$C_3D_3^+$	8.56	8.51	9.32	9.73	9.28	9.49	8.72	7.97	7.03	5.68	3.96	1.37	0.43
41	$C_3D_2H^+$	25.36	25.25	24.87	27.11	23.56	21.49	21.30	17.34	14.14	11.25	7.78	3.02	1.08
40	$C_3D_2^+$	5.62	6.06	6.00	4.93	1.39	1.13	0.80	0.44	0.21	0.12	0.11
39	C_3DH^+	6.61	6.67	6.94	5.73	2.20	1.78	1.23	0.78	0.43	0.29
38	C_3D^+	6.61	6.29	4.10	1.43	0.13	0.01	0.01
37	C_3H^+	1.81	1.75	1.28	0.52	.04
36	C_3^+	2.09	1.61	0.23	.02	.01
30	$C_3D_3^+$	0.22	0.23	.21	.11	.03	.03	.02	.01	.01
29	$C_2D_2H^+$.12	.14	.13	.06	.02	.02	.01	.01
28	$C_2D_2^+$	1.16	.91	.53	.17	.03	.02	.005
27	C_2DH^+	.41	.41	.27	.13	.005	.06
26	C_2D^+	1.15	.91	.24	.09
25	C_2H^+	.70	.70	.32	.21	.07
24	C_2^+	.57	.31	.07

TABLE IIb
MASS SPECTRUM OF PROPYNE- d_3 (SIMPLIFIED)

Ion	Electron accelerating potential (volts)												
	50	40	30	25	20	19	18	17	16	15	14	13	12
$C_3D_3H^+$	38.81	40.23	45.45	49.71	63.21	65.94	67.88	73.40	78.14	82.62	88.15	95.60	98.47
$C_3D_3^+ + C_3D_2H^+$	34.92	33.73	34.19	36.84	32.84	30.98	30.02	25.31	21.17	16.93	11.74	4.39	1.51
$C_3D_2^+ + C_3DH^+$	12.23	12.73	12.94	10.66	3.59	2.91	2.03	1.22	0.64	0.41	0.11
$C_3D^+ + C_3H^+$	8.42	8.04	5.38	1.95	0.17	0.01	0.01
C_3^+	2.05	1.61	0.23	0.02	.01
$C_3D_3^+ + C_2D_2H^+$	0.36	0.37	.34	.17	.05	.05	.03	0.02	0.01
$C_2D_2^+ + C_2DH^+$	1.57	1.32	.80	.30	.03	.08
$C_2D^+ + C_2H^+$	1.85	1.61	.56	.30	.07
C_2^+	0.57	0.31	.07

peaks. These ions are formed by the loss of a H-atom and a D-atom, respectively, and the processes which might be expected would be



Since the energies and frequency factors involved in these two processes should be quite different, it is surprising to find that the probabilities of loss of H and of D correspond almost exactly to the statistical probabilities. The removal of two and three atoms also seems to proceed on a statistical basis. This is clearly shown by the ionic ratios of $C_3D_3^+/(C_3D_2H^+ + C_3D_3^+)$, $C_3D_2^+/(C_3DH^+ + C_3D_2^+)$, and $C_3D^+/(C_3H^+ + C_3D^+)$ given in Table III, the ratios being nearly $1/4$, $2/4$ and $3/4$, respectively. This is especially true at the higher electron energies. At lower electron energies the ratios increase appreciably,

particularly the ratio $C_3D_2^+/(C_3DH^+ + C_3D_2^+)$, although the change is perhaps not much greater than would be expected to result from the increasing importance of zero point energy differences between C-H and C-D bonds as the available energy is reduced.

Further evidence for the equivalence of the H and D atoms can be obtained from the appearance potentials of the $C_3D_3^+$ and $C_3D_2H^+$ ions as given in Table IV. Using these data and the quantities $\Delta H_f(\text{propyne}) = 44.32 \text{ kcal./mole}^{4a}$ and $\Delta H_f(H) = 52.1 \text{ kcal./mole}^{4b}$ the following heats of formation are obtained

$$\begin{aligned} \text{from } C_3H_4, \Delta H_f(C_3H_3^+) &= 270.2 \text{ kcal./mole} \\ \text{from } C_3D_3H, \Delta H_f(C_3D_2H^+) &= 274.0 \text{ kcal./mole} \\ \text{from } C_3D_3H, \Delta H_f(C_3D_3^+) &= 272.7 \text{ kcal./mole} \end{aligned}$$

(4) (a) F. D. Rossini, *et al.*, "Selected Values, etc.," Carnegie Press, Pittsburgh, Pa., 1953; (b) F. D. Rossini, *et al.*, Circular 500, National Bureau of Standards, Washington, D. C., 1952.

TABLE III
 IONIC ABUNDANCE RATIOS

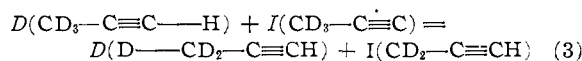
Ratio of ions	50	40	30	25	Electron accelerating potential (volts)								
					20	19	18	17	16	15	14	13	12
$C_3D_3/(C_3D_2H + C_3D_3)$	0.245	0.252	0.273	0.264	0.282	0.306	0.291	0.315	0.332	0.335	0.337	0.312	0.285
$C_3D_2/(C_3DH + C_3D_2)$.460	.524	.536	.538	.613	.612	.606	.639	.672	.707
$C_3D/(C_3H + C_3D)$.785	.782	.763	.733	.765

TABLE IV

APPEARANCE POTENTIALS

Potential	Propyne	Propyne- d_3
Ionization potential	10.54 ± 0.03	10.62 ± 0.05
$A(C_3H_3^+)$	$12.06 \pm .06$
$A(C_3D_3^+)$	$12.16 \pm .06$
$A(C_3D_2H^+)$	$12.22 \pm .05$

These three values are essentially the same within the experimental error and are in fair agreement with earlier values for $\Delta H_f(C_3H_3^+)$.^{2,5} This means that the energy difference to be expected if processes 1 and 2 are the modes of formation of $C_3D_3^+$ and $C_3D_2H^+$, respectively, is not found. Two possibilities may be considered: first, that the expected energy difference is actually zero, and that



That is, the difference in bond dissociation energies is exactly compensated by the difference in ionization potential of the radicals. This coincidence seems extremely unlikely, particularly since both quantities on the left-hand side of equation 3 would be expected to be considerably larger than the corresponding quantities on the right-hand side. Alternatively, one must conclude that the $C_3D_3^+$ and $C_3D_2H^+$ ions have the same structure, and that the necessary rearrangement of H and D atoms in the propyne ion can proceed very easily prior to dissociation.

Numerous cases of such rearrangements have been reported in the literature as resulting from impact by 30 or 75 v. electrons, but in very few cases have the energy thresholds for such rearrangements been measured. Stevenson⁶ concluded from a study of the energies of formation of alkyl ions from hydrocarbons that *n*-alkyl ions were isomerized to *sec*-alkyl ions, at least in some cases, during the dissociation process. The case reported here is rather similar.

(5) F. H. Coats and R. C. Anderson, THIS JOURNAL, **79**, 1340 (1957).

(6) D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 867 (1953).

It is possible to show that very little energy is available for activation of the rearrangement process in propyne ion. It is, of course, not sufficient to show that the heat of formation of the rearranged ion $C_3D_3^+$ from CD_3CCH is the same as for the $C_3D_2H^+$ ion, since both processes might involve an excess energy term which would be available for the rearrangement. There are good reasons, however, for believing that the excess energy term is small or zero. The appearance potentials for the $C_3H_3^+$ ion from propyne as reported here and in earlier publications^{1,5} lead to an average value for $\Delta H_f(C_3H_3^+)$ of about 269 kcal./mole. Assuming this to be the propargyl ion, for which the ionization potential is 8.25 ± 0.08 v.² and using the value $\Delta H_f(\text{propyne}) = 44.32$ kcal./mole,³ it follows that

$$D(HC\equiv C-CH_2-H) + E = 87 \text{ kcal./mole} \quad (4)$$

where E is any excess energy involved in the process. It seems almost certain from structural considerations that this bond must be stronger than $D(\text{allyl-H})$ which is quite well established as 78–79 kcal./mole.^{7,8} The upper limit for the excess energy term E in equation 4 available as activation energy for the rearrangement of H atoms is consequently about 9 kcal./mole. If, as one might reasonably expect, $D(HC\equiv C-CH_2-H)$ is actually several kcal./mole greater than $D(\text{allyl-H})$, the energy available for activation of the rearrangement becomes very small indeed.

As for the ionization potentials of propyne and propyne- d_3 given in Table IV, it is questionable whether the difference of 0.08 v. represents a significant isotopic difference in vertical ionization potential, as has been found for methane^{9,10} and ammonia.¹¹

OTTAWA, CANADA

(7) M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

(8) C. A. McDowell, F. P. Lossing, I. H. S. Henderson and J. B. Farmer, *Can. J. Chem.*, **34**, 345 (1956).

(9) R. E. Honig, *J. Chem. Phys.*, **16**, 105 (1948).

(10) F. P. Lossing, A. W. Tickner and W. A. Bryce, *ibid.*, **19**, 1254 (1951).

(11) H. Neuert, *Z. Naturforschung*, **7a**, 293 (1952).