oxalate, citrate, phosphate, phthalate and bicarbonate buffers have been determined.

Attempts to determine the composition of the complex in acetate buffers gave anomalous results. Oxalate, citrate and phosphate destroyed the complex. Tests in phthalate and bicarbonate buffers indicated a 1:1 complex, up to pH 7.75.

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Mass Spectrometric Analysis of Low-molecular-weight Monodeutero-paraffins

BY D. P. STEVENSON AND C. D. WAGNER

The analysis of monodeutero-paraffins prepared in this Laboratory[1] (all eight of the mono-deutero-alkanes, C_1–C_4) presents certain problems which have been solved successfully by the use of mass spectrometric techniques. The general applicability of these techniques has made it desirable to treat these aspects in a paper separate from that dealing with the preparation and purification of the compounds.

The mass spectrometer provides a sensitive means of detecting impurities in volatile substances, provided the impurities have molecular weights greater than the molecular weight of the substance under investigation or, more generally, are of such a nature that they produce ions not coincident in mass–charge ratio with those of the substance under investigation. In general for impurities of molecular weight less than the substance under investigation to be determinable by the ordinary mass spectrometric analytical methods, a "pure" or standard sample must be available for comparison purposes. Such standard samples of monodeuteroparaffins are not available and ordinary methods of standardization are not applicable. For the determination of olefin and ordinary (undeuterated) alkane in the deutero-hydrocarbons, special methods were devised. These methods and the results obtained are described below. No description of the detection of impurities of higher molecular weight by the mass spectrometric technique is given here since these are adequately described in the literature.[2]

Determination of Olefins.—As has been discussed in another recent paper,[1] a characteristic side reaction in the synthesis of a paraffin by hydrolysis of a Grignard reagent leads to the formation of equal amounts of olefin and undeuterated paraffin. Since certain reactions of paraffins are very sensitive to trace olefin impurities,[3] sensitive analytical methods are necessary to check the efficacy of chemical treatments employed to remove the olefins. In addition to having high sensitivity, the methods must consume a

very small sample, or be non-destructive, since the deuteroalkanes are laboratory preparations prepared on small scale.

In principle, infrared absorption is applicable to this problem. Rasmussen and Brattain[4] have observed that monoölefins, in general, have very strong characteristic absorption bands in the region 10–12.5 μ where the corresponding paraffins have relatively very weak absorption. To the extent that monodeutero-paraffins do not differ significantly in their absorption in this region from that of the ordinary paraffins, infrared absorption measurements should afford considerable sensitivity to detection of olefins. However, for even the simple monodeutero-paraffins considered in this paper, it is found that characteristic absorption bands do appear in this region (10–12.5μ) which render the method inapplicable in the absence of authentic standards for comparison.[5]

Since the infrared method of olefin detection was found to be inapplicable, it was deemed desirable to develop a potentially absolute mass spectrometric method for olefin estimation in both paraffins and monodeutero-paraffins. This method is described in the following paragraphs.

Owing to the nature of the ionization process, the appearance potential of the ion-fragment, $C_nH_{2n}^+$, in the mass spectrum of the paraffin, $C_nH_{2n}^{+}{}_2$, or $C_nH_{2n+1}D$, is necessarily 1.1 to 1.4 ev. greater than the appearance potential of the ion, $C_nH_{2n}^+$, in the mass spectrum of the olefin, C_nH_{2n}. This follows from the fact that the appearance potential of $C_nH_{2n}^+$ in the mass spectrum of $C_nH_{2n}^{+}{}_2$ or $C_nH_{2n+1}D$ is greater than or equal to the ionization potential of the olefin, C_nH_{2n}, plus the heat of dehydrogenation of the paraffin, $C_nH_{2n}^{+}{}_2$ or $C_nH_{2n+1}D$, while the appearance potential of $C_nH_{2n}^+$ in the mass spectrum of the olefin C_nH_{2n} is approximately equal to the ionization potential of the olefin, C_nH_{2n}. The heats of dehydrogenation of the C_2–C_4 paraffin lie between +27 and +33 kcal./mole or 1.2–1.4 ev.[6] Thus, it should be possible to measure the

(1) C. D. Wagner and D. P. Stevenson, THIS JOURNAL, **72**, 5784 (1950). The deuterium oxide used in the syntheses was supplied by Stuart Oxygen Company on allocation from the Isotopes Division, U. S. Atomic Energy Commission.

(2) H. W. Washburn, H. F. Wiley and S. M. Rock, *Ind. Eng. Chem., Anal. Ed.*, **15**, 541 (1943).

(3) R. C. Wackher and H. Pines, THIS JOURNAL, **68**, 1642, 2518 (1946).

(4) R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 120 (1940).

(5) The authors are indebted to various colleagues, particularly Dr. F. S. Mortimer for infrared absorption measurements on the various C_1–C_4 monodeutero-paraffins. A detailed account of the infrared absorption of these substances will be published at a later date.

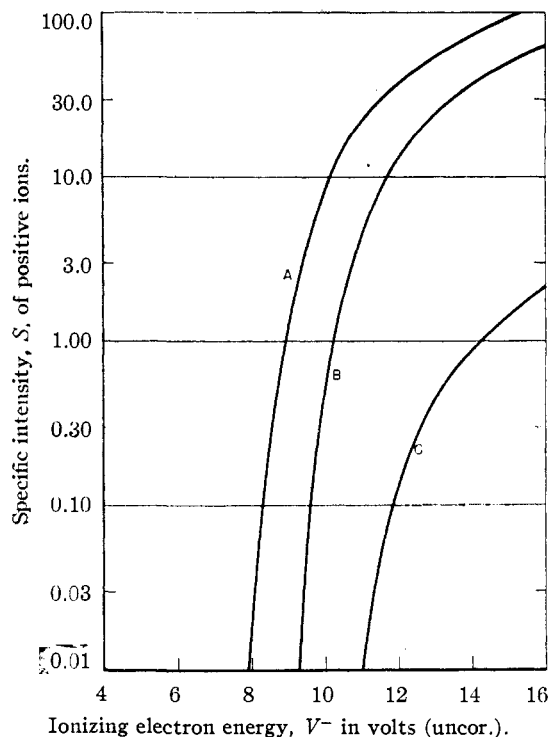(6) Kistiakowsky, *et al.*, THIS JOURNAL, **57**, 65, 876 (1935)

Fig. 1.—Ionization efficiency curves of the methane ions, $CH_4{}^+$, $CH_3{}^+$ and $CH_2{}^+$. The specific intensities at $V^- = 75$ volts are $CH_4{}^+ = 348$, $CH_3{}^+ = 261$ and $CH_2{}^+ = 25.8$. To correct voltage scale, V^-, to an absolute basis add 4.1 e. v. in this figure and Figs. 2–5. (A) $CH_4 \rightarrow CH_4{}^+ + \epsilon^-$, (B) $CH_4 \rightarrow CH_3{}^+ + H + \epsilon^-$, (C) $CH_4 \rightarrow CH_2{}^+ + H_2 + \epsilon^-$.

Fig. 2.—Ionization efficiency curves of the ethane ions, $C_2H_6{}^+$, $C_2H_5{}^+$ and $C_2H_4{}^+$, and the ethylene ion, $C_2H_4{}^+$. The specific intensities at $V^- = 75$ volts are: ethane, $C_2H_6{}^+ = 250$, $C_2H_5{}^+ = 167$, and $C_2H_4{}^+ = 784$; ethylene, $C_2H_4{}^+ = 572$. The specific intensity of $C_2H_5{}^+$ from ethane has been corrected for contribution from the ion $C^{12}C^{13}H_4{}^+$ due to the natural C^{13} content of the ethane (see legend to Fig. 1). (A) $C_2H_4 \rightarrow C_2H_4{}^+ + \epsilon^-$, (B) $C_2H_6 \rightarrow C_2H_4{}^+ + H_2 + \epsilon^-$, (C) $C_2H_6 \rightarrow C_2H_6{}^+ + \epsilon^-$, (D) $C_2H_6 \rightarrow C_2H_5{}^+ + H + \epsilon^-$.

mass spectrum of the paraffin preparation at such an electron energy that the only source of ions $C_nH_{2n}{}^+$ in the mass spectrum will be C_nH_{2n} impurity.

In Figs. 2 through 5 there are shown the variation of specific intensity (sensitivity) of the ions $C_nH_{2n+2}{}^+$, $C_nH_{2n+1}{}^+$ and $C_nH_{2n}{}^+$ in the mass spectra of the paraffins, C_nH_{2n+2}, $2 \leqslant n \leqslant 4$ and $C_nH_{2n}{}^+$ in the mass spectra of the olefins C_nH_{2n}, $2 \leqslant n \leqslant 4$, with ionizing electron energy in the vicinity of the appearance potentials of these ions. In these figures, the specific intensities are in arbitary units such that 0.01 unit is the minimum detectable signal. The specific intensity units are the same for all substances. The ionizing electron energy scale is in volts, uncorrected for contact potentials, field penetration or contributions from the positive ion drawing out field characteristic of the Westinghouse Type LV mass spectrometer. From the appropriate curves in these figures, it follows that the absolute limits of detection of the various olefins in the corresponding paraffins are: 0.25% C_2H_4 in C_2H_6 measured at 6.5 volts, 0.05% C_3H_6 in C_3H_8 measured at 6.0 volts and 0.01% C_4H_8 in C_4H_{10} measured at 6.0 volts. If the standard paraffins contain any olefin, then the above limits would be correspondingly reduced.

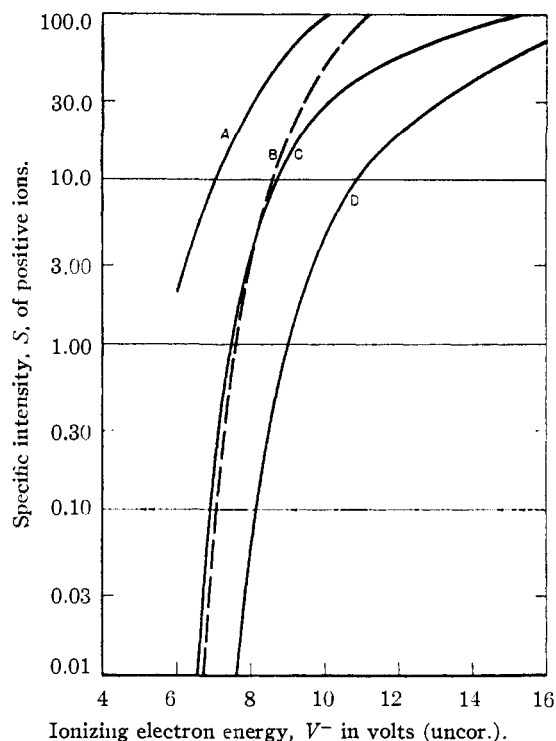In the case of the deutero-paraffins, the limits of detection of C_nH_{2n} should be lower than those quoted for the ordinary paraffins since the formation of $C_nH_{2n}{}^+$ from $C_nH_{2n+1}D$ requires the removal of HD from the molecule-ion, a process of lower intrinsic probability than that of removal of H_2 from C_nH_{2n+2}, and thus the specific intensity

TABLE I

ANALYSES OF MONODEUTERO-PARAFFINS

	Mole % C_nH_{2n} M. S.	M. S.[a]	Mole % C_nH_{2n+2} M. S.[b]	M. S.[c]	I. R.[d]
CH_4-d_1	..	4.0 ± 0.5	4.2 ± 0.5	....	...
C_2H_6-d_1	0.1	....	2.3 ± 1.0	....	...
C_3H_8-1-d_1	.03	....	....	2.1 ± 1.0	...
C_3H_8-2-d_1	.03	....	....	1.0 ± 1.0	<2
n-C_4H_{10}-1-d_1	.01	....	0.5 ± 0.4	....	...
n-C_4H_{10}-2-d_1	.01	....	2.0 ± 0.4	....	...
i-C_4H_{10}-1-d_1	.01	....	2.0 ± 1.0	....	...
i-C_4H_{10}-2-d_1	.02	....	0.5 ± 0.2	....	...

[a] Method 1: Conversion to H_2, HD and D_2 and mass spectral analysis of latter mixture. [b] Method 2: Measurement of the mass spectrum at an ionizing electron energy less than the effective appearance potential of $C_nH_{2n+1}{}^+$ in the C_nH_{2n+2} mass spectrum. [c] Method 3: Curve fitting, equation (4) of text. [d] Infrared absorption spectra. See text and Fig. 6.

of $C_nH_{2n}{}^+$ in the $C_nH_{2n+1}D$ mass spectrum should always be less than that of $C_nH_{2n}{}^+$ in the C_nH_{2n+2} mass spectrum. This expectation was realized in the cases of ethylene in ethane-d and propylene in both propane-1-d and propane-2-d as may be seen in column 2 of Table I, where the limits to the olefin content of the various monodeutero-paraffin preparations, determined by this mass spectrometric method, are given.
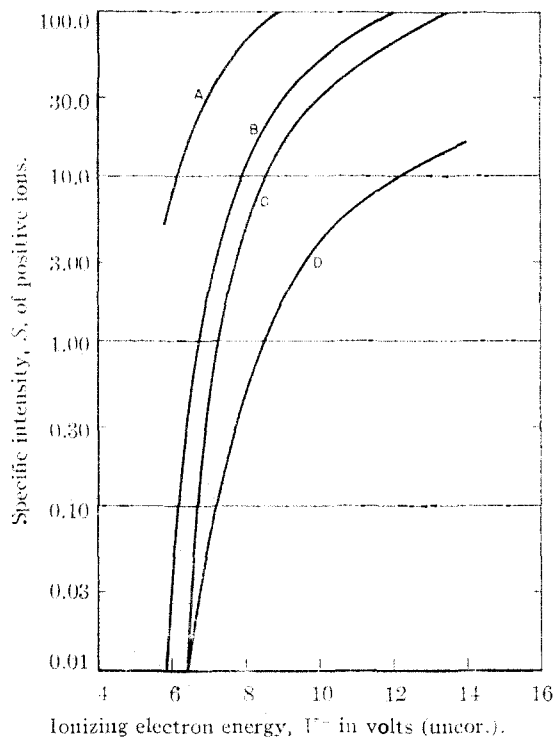

Fig. 3.—Ionization efficiency curves of the propane ions, $C_3H_8{}^+$, $C_3H_7{}^+$ and $C_3H_6{}^+$ and the propylene ion $C_3H_6{}^+$. The specific intensities at $V^- = 75$ volts are: propane, $C_3H_8{}^+ = 310$, $C_3H_7{}^+ = 240$ and $C_3H_6{}^+ = 44.4$; propylene, $C_3H_6{}^+ = 362$ (see legend to Fig. 1). (A) $C_3H_6 \rightarrow C_3H_6{}^+ + \epsilon$, (B) $C_3H_8 \rightarrow C_3H_8{}^+ + \epsilon$, (C) $C_3H_8 \rightarrow C_3H_7{}^+ + H + \epsilon^-$, (D) $C_3H_8 \rightarrow C_3H_6{}^+ + H_2 + \epsilon^-$.

From the curves of Figs. 3 through 5, it is possible to draw certain conclusions with regard to the purity of Phillips Certified propane, n-butane and isobutane; these substances were used throughout this investigation as reference standards. The limits quoted for the limit of detection of propylene in propane, 0.05%, and butylene in butane, 0.01%, are the upper limits to the possible concentrations of these impurities.

In concluding this discussion of the estimation of the olefin content of monodeutero-paraffins, it should be remarked that with increasing carbon number, the method loses no sensitivity. This results from the fact that for C_5 and higher paraffins, the probability of the electron impact induced process
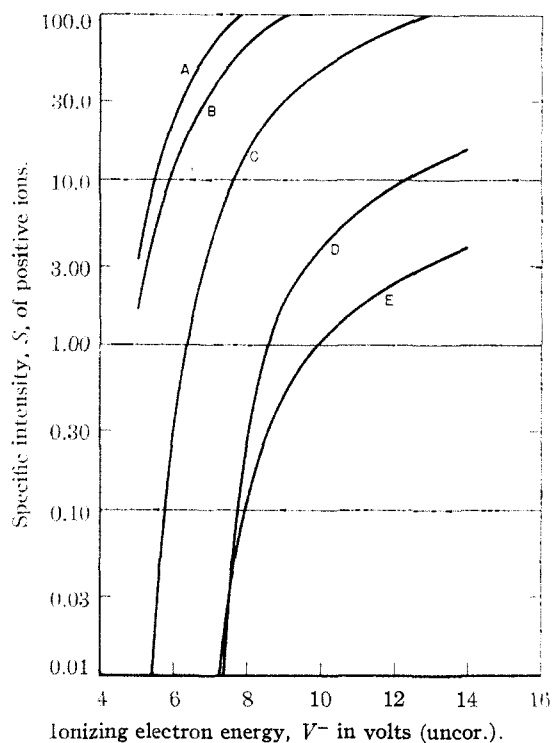
$$C_nH_{2n+2} + \epsilon^- \longrightarrow C_nH_{2n}{}^+ + H_2 + 2\epsilon^-$$

Ionizing electron energy, V^- in volts (uncor.).

Fig. 4.—Ionization efficiency curves of the n-butane ions, $C_4H_{10}{}^+$, $C_4H_9{}^+$ and $C_4H_8{}^+$ and the α- and cis-β-butylene ions, $C_4H_8{}^+$. The specific intensities at $V^- = 75$ volts are: n-butane, $C_4H_{10}{}^+ = 220$, $C_4H_9{}^+ = 30.0$, $C_4H_8{}^+ = 8.24$; α-butylene, $C_4H_4{}^+ = 290$; cis-β-butylene, $C_4H_8{}^+ = 330$ (see legend to Fig. 1). (A) cis-β-$C_4H_8 \rightarrow C_4H_8{}^+ + \epsilon^-$, (B) α-$C_4H_8 \rightarrow C_4H_8{}^+ + \epsilon^-$, (C) n-$C_4H_{10} \rightarrow C_4H_{10}{}^+ + \epsilon^-$, (D) n-$C_4H_{10} \rightarrow C_4H_9{}^+ + H + \epsilon^-$, (E) n-$C_4H_{10} \rightarrow C_4H_8{}^+ + H_2 + \epsilon^-$.

becomes less and less, while the relative forms of the pertinent ionization efficiency curves do not change. Comparison in this Laboratory of ionization efficiency curves of $C_6H_{12}{}^+$ of several 2-methylpentenes with that of the ion $C_6H_{12}{}^+$ in the 2-methylpentane mass spectrum reveals the limit of detection of C_6 olefin in 2-methylpentane (and its monodeuterides) to be 0.03%.

Determination of Undeuterated Alkanes.—Preparations of the monodeuteroparaffins always contain as an impurity ordinary paraffins which may arise from (1) hydrogen impurity in the source deuterium, (2) accidental hydrogen contamination, and (3) ordinary paraffin formed along with olefin in the disproportionation reaction of the Grignard reagent. The last named source of ordinary paraffin is most serious since it is less subject to control and since the extent of contamination from such a disproportionation reaction is essentially unpredictable for any given Grignard reagent. Several methods may be used to determine the resultant C_nH_{2n+2} impurity of a preparation of $C_nH_{2n+1}D$.

A rather laborious, but always applicable, method of determining the C_nH_{2n+2} content of a

preparation of $C_nH_{2n+1}D$ is to convert all of the hydrogen atoms of a portion of the sample to a mixture of H_2, HD and D_2, and then determine the relative concentration of the isotopic hydrogens and thus the atomic ratio of H to D in the preparation. A simple calculation permits the estimation of the C_nH_{2n+2}, provided this is the only hydrogen-containing impurity of the preparation. If α is the mole fraction C_nH_{2n+2} and $1-\alpha$ the mole fraction of $C_nH_{2n+1}D$, then

$$\frac{D}{H} = \frac{D_2 + \frac{1}{2}HD}{\frac{1}{2}HD + H_2} = \frac{1-\alpha}{2n+1+\alpha}$$

or

$$\alpha = [1 + (2n+1)(D/H)]/[1 + (D/H)]$$

The most convenient method for completely converting a hydrocarbon to hydrogen is to expose the hydrocarbon to metallic chromium at temperatures between 800 to 1000°. The large free energy of formation of the chromium carbides, Cr_5C_2 and Cr_3C_2[7] assures the essential completeness of the reactions

$$5nCr + 2C_nH_{2n+2} \longrightarrow nCr_5C_2 + (2n+2)H_2 \text{ or}$$
$$3nCr + 2C_nH_{2n+2} \longrightarrow nCr_3C_2 + (2n+2)H_2$$
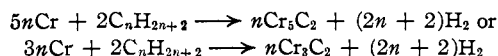
This method of conversion of hydrocarbon to hydrogen is preferable to combustion to water from which the hydrogen may be generated for analysis because it avoids the danger of exchange of D for H between water and strongly adsorbed ordinary water on vessel walls and other surfaces. The mass spectrometer gives a reasonably accurate analysis of the resultant H_2, HD and D_2 mixture and the mass spectrum permits a sensitive measure of the completeness of the conversion of the hydrocarbon to hydrogen as well.

The above described method was applied to the analysis of the methane-d sample and gave 4.0 ± 0.5% CH_4 in the CH_3D. In the case of higher monodeutero-paraffins, the method, and any method depending upon determination of the gross D/H ratio, suffers from the high dilution of the deuterium by the $2n+1$ hydrogens present and thus tends to require an increasingly accurate measurement of the composition of the H_2, HD and D_2 mixtures.

A second method in the case of the monodeutero-paraffins of determining the C_nH_{2n+2} content of $C_nH_{2n+1}D$ samples is one that uses the same principles as that of the mass spectrometric method of determining olefin impurity. The appearance potential of the ion $C_nH_{2n+1}^+$ in the mass spectrum of C_nH_{2n+2} and hence the appearance potential of $C_nH_{2n}D^+$ in the mass spectrum of $C_nH_{2n+1}D$ is greater than the appearance potential of $C_nH_{2n+2}^+$ in the mass spectrum of C_nH_{2n+2} by 1 to 2 volts, $i.\ e.$, by the difference between the dissociation energy of the first C–H bond of $C_nH_{2n+2}^+$ and the difference between the vertical and adiabatic ionization potential
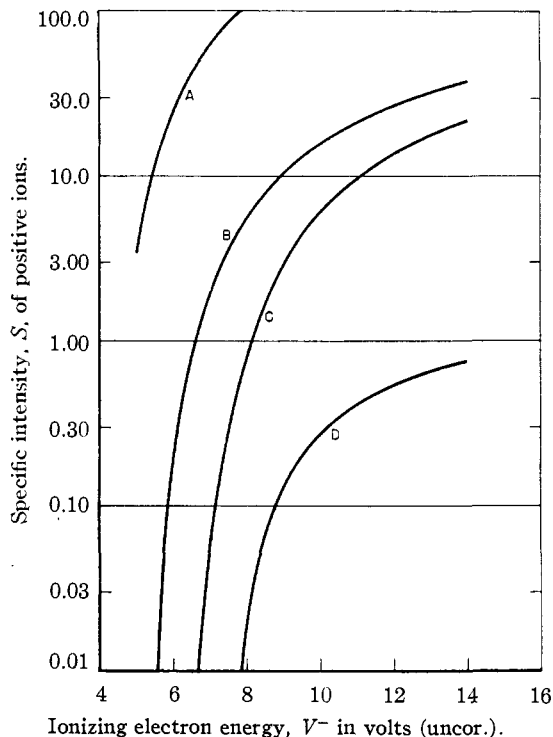
Fig. 5.—Ionization efficiency curves of the i-butane ions, $C_4H_{10}^+$, $C_4H_9^+$ and $C_4H_8^+$, and the isobutylene ion $C_4H_8^+$. The specific intensities at $V^- = 75$ volts are, isobutane $C_4H_{10}^+ = 71.6$, $C_4H_9^+ = 45.3$, $C_4H_8^+ = 5.32$; isobutylene, $C_4H_8^+ = 333$ (see legend to Fig. 1). (A) i-$C_4H_8 \rightarrow C_4H_8^+ + \epsilon^-$, (B) i-$C_4H_{10} \rightarrow C_4H_{10}^+ + \epsilon^-$, (C) i-$C_4H_{10} \rightarrow C_4H_9^+ + H + \epsilon^-$, (D) i-$C_4H_{10} \rightarrow C_4H_8^+ + H_2 + \epsilon^-$.

of C_nH_{2n+2}.[8] Thus, the mass spectrum of a monodeutero-paraffin sample may be measured at such an ionizing electron energy that the only source of ion of $m/q = 14n + 2$ (corresponding to C_nH_{2n+2} or $C_nH_{2n}D^+$) is the C_nH_{2n+2} content of the $C_nH_{2n+1}D$. In Fig. 1 through 5 the course of the pertinent ionization efficiency curves for the five C_1–C_4 paraffins is shown.

Examination of the figures referred to reveals that the limits of detection of C_nH_{2n+2} in $C_nH_{2n+1}D$ by the method outlined in the preceding paragraph are: $ca.$ 0.3% CH_4 in CH_3D with 9 volt electrons, $ca.$ 1.0% C_2H_6 in C_2H_5D with 7 volt electrons, $ca.$ 0.4% n-C_4H_{10} in n-$C_4H_{10}D$ with 7 volt electrons and $ca.$ 1.0% i-C_4H_{10} in i-C_4H_9D with 6 volt electrons, if it is assumed that the course of the ionization efficiency curve of $C_nH_{2n}D^+$ in the $C_nH_{2n+1}D$ mass spectrum is essentially coincident with that of $C_nH_{2n+1}^+$ in the C_nH_{2n+2} mass spectrum. The very near equality of the appearance potentials of $C_3H_7^+$ and $C_3H_8^+$ in the propane mass spectrum renders this method inapplicable to C_3H_7D samples. It may be noted in passing that the much larger difference between the appearance potential of $C_nH_{2n-3}^+$ and C_n-

(7) K. K. Kelly, Bureau of Mines Bulletin 407, 1937, pp. 10 and 11.

(8) See Koffel and Lad, $J.\ Chem.\ Phys.,$ **16**, 420 (1948), for a summary of appearance potentials in the mass spectra of paraffins.

H_{2n-2}^+ (acetylenes) and $C_nH_{2n-1}^+$ and $C_nH_{2n}^+$ (olefins) than for $C_nH_{2n+1}^+$ and $C_nH_{2n+2}^+$ (paraffins) results in this method having much greater sensitivity for the determination of C_nH_{2n-2} in $C_nH_{2n-3}D$ or C_nH_{2n} in $C_nH_{2n-1}D$ than is the case for C_nH_{2n+2} in $C_nH_{2n+1}D$. For instance, 0.05% C_2H_2 is readily detected in either C_2HD or C_2D_2 by this method.

Through measurements of the mass spectra at the above indicated ionizing electron energies the estimates of the C_nH_{2n+2} content of the $C_nH_{2n+1}D$, methane-d, ethane-d, n-butane-1-d, n-butane-2-d, i-butane-1-d and i-butane-2-d, shown in column 4 of Table I, were obtained. It will be noted that in the case of i-butane-2-d the sensitivity is greater than that predicted from the curves of Fig. 5. This results from the very low probability of dissociation of a primary hydrogen by an isobutane ion.[9] As a result, the specific intensity of the ion of $m/q = 58$ in the mass spectrum of isobutane-2-d is very small (compared to that of this ion in the mass spectrum of isobutane-1-d or the ion $m/q = 57$ of isobutane-d_0) and becomes less than the limit of measurement at a higher ionizing electron energy than does 58 or 57 for isobutane-1-d or isobutane-d_0, respectively.

A third method, which like the second method for determination of C_nH_{2n+2} in $C_nH_{2n+1}D$ depends upon measurements of the mass spectra at low ionizing electron energies, is also available. It is well known that the specific intensities of most ions in the mass spectra of hydrocarbons are linear functions of the ionizing electron energy over a limited range of the ionizing energy. This range, for such ions as $C_nH_{2n+2}^+$ and $C_nH_{2n+1}^+$, starts 1.5 to 2.0 volts above the appearance potential of the ion and continues for 6–10 volts, or until the specific intensity has attained $ca.$ 50–60% of the maximum value characteristic of ionizing energies between 50 and 100 volts. It is further known that for similar processes, the intercept of the extrapolated linear portion of the ionization efficiency curve on the ionizing energy axis is a measure of the appearance potential.[10] Thus, over the range of ionizing electron energies for which the specific intensities of both $C_nH_{2n+2}^+$ and $C_nH_{2n+1}^+$ are linear functions of the ionizing energy, the ratio of intensities, $C_nH_{2n}D^+/C_nH_{2n+1}D^+$ in the mass spectrum of pure $C_nH_{2n+1}D$, will be equal to a constant, independent of the ionizing electron energy, times the ratio of intensities $C_nH_{2n+1}^+/C_nH_{2n+2}^+$ in the mass spectrum of pure C_nH_{2n+2}. This may be proved as follows: If the specific intensities of $C_nH_{2n}D^+$, $C_nH_{2n+1}D^+$, $C_nH_{2n+1}^+$ and $C_nH_{2n+2}^+$

(9) D. P. Stevenson and C. D. Wagner, *J. Chem. Phys.*, in publication.

(10) For discussions of the significance of ionization efficiency curves and their interpretation, see: Stevenson, *J. Chem. Phys.*, **10**, 291 (1942); Stevenson and Hipple, *Phys. Rev.*, **62**, 237 (1942); Mariner and Bleakney, *ibid.*, **72**, 807 (1947); Vought, *ibid.*, **71**, 93 (1947).

are i^d_{-1}, i^d_0, i^h_{-1} and i^h_0, respectively, for the pure compounds, α^d_{-1}, α^d_0, α^h_{-1} and α^h_0 are the slopes of the linear portion of their ionization efficiency curves, and I^d_{-1}, I^d_0, I^h_{-1} and I^h_0 the corresponding intercepts with the ionizing electron energy (V^-) axis, then, over the range of V^- for which the i's are linear

$$
\begin{aligned}
i^d_{-1} &= \alpha^d_{-1}(V^- - I^d_{-1}) \\
i^d_0 &= \alpha^d_0(V^- - I^d_0) \\
i^h_{-1} &= \alpha^h_{-1}(V^- - I^h_{-1}) \\
i^h_0 &= \alpha^h_0(V^- - I^h_0)
\end{aligned}
\tag{1}
$$

and

$$
[C_nH_{2n}D^+/C_nH_{2n+1}D^+]/[C_nH_{2n+1}^+/C_nH_{2n+2}^+] =
$$
$$
(i^d_{-1}/i^d_0)/(i^h_{-1}/i^h_0) = \frac{\alpha^d_{-1}}{\alpha^d_0} \times \frac{\alpha^h_0}{\alpha^h_{-1}} \times \frac{V^- - I^d_{-1}}{V^- - I^h_{-1}} \times
$$
$$
\frac{V^- - I^h_0}{V^- - I^d_0} \tag{2}
$$

The intercepts, I, are measures of the appearance potentials, I^d_{-1} and I^h_{-1}, and I^d_0 and I^h_0, which will only differ through differences in the zero point energies of the initial and final states, $i.\,e.$, by the order of 0.02–0.05 e.v. The appearance potentials themselves are of the order of 10 to 12 e.v.; thus, $V^- - I^d_{-1}/V^- - I^h_{-1}$ and $V^- - I^h_0/V^- - I^d_0$, will each differ from unity by 0.5% at most and probably in opposite sense. Thus

$$
[C_nH_{2n}D^+/C_nH_{2n+1}D^+]/[C_nH_{2n+1}^+/C_nH_{2n+2}^+] =
$$
$$
\frac{\alpha^d_{-1}}{\alpha^d_0} \times \frac{\alpha^h_0}{\alpha^h_{-1}} = \Gamma \tag{3}
$$

where Γ is a constant to better than $\pm 0.5\%$ over the specified range of V^-.

As a consequence of the above, over the specified range of V^-, the specific intensity i_m of the ion, $m/q = 14n + 2$, corresponding to $C_nH_{2n+2}^+$ plus $C_nH_{2n}D^+$ in the mass spectrum of the $C_nH_{2n+1}D$ preparation can be written

$$
i_m = S^h_m[P - H] + \Gamma \rho_{m-1} i_{m+1} \tag{4}
$$

where S^h_m, $[P - H]$ and ρ_{m-1} are, respectively, the specific intensity of $C_nH_{2n+2}^+$ characteristic of pure C_nH_{2n+2}, the mole fraction of C_nH_{2n+2}, and the characteristic ratio, $C_nH_{2n+1}^+/C_nH_{2n+2}^+$, and i_{m+1} is the specific intensity of the ion, $m/q = 14n + 3$, corresponding to $C_nH_{2n+1}D^+$. From measurements of the mass spectra of pure C_nH_{2n+2} and the sample of $C_nH_{2n+1}D$ at two ionizing electron energies, V_1^- and V_2^-, in the specified range of V^-, there are obtained a pair of simultaneous equations in the two unknowns, $[P - H]$ and Γ. In order for the pair of equations to be solvable, the available range of V^- is subject to the further conditions that S_m and ρ_{m-1} have different rates of change with V^-.

In the case of propane, the ionization efficiency curves for $C_3H_8^+$ and $C_3H_7^+$ are both linear for $9.0 \leqslant V^- \leqslant 16.0$ e.v. (uncorrected scale corresponding to Figs. 1 through 5) and dS_{44}/dV^- and $d\rho_{43}/dV^-$ differ most in the range $9.0 \leqslant V^- \leqslant 12.0$ e.v. Thus measurements of i_{44} and i_{45} for the propane-1-d and propane-2-d samples were made at 0.5 e.v. intervals over $9.0 \leqslant V^- \leqslant$

12.0. The resultant sets of simultaneous equations were solved by the usual least squares methods to give "best values" of the C_3H_8 content and Γ for each propane-d. The values of the C_3H_8 content so obtained and an estimate of the probable uncertainty is given in column 5 of Table I.

In the course of obtaining data for the analysis of the methane-d, ethane-d and butane-d samples, sufficient data were obtained to test the constancy of Γ over the applicable ranges of V^- for these substances. The values of Γ were calculated by means of equation (4) and the mole fraction, [P − H], obtained from the first or second method. In all cases, Γ was found to be constant to $\pm 2\%$, a reasonable estimate of the experimental errors.

The infrared absorption spectra of the seven substances described in this paper were observed in the rocksalt region, 3–14μ. A complete description of these spectra will be the subject of a separate communication.[11] A peculiarity of this absorption spectrum of propane-2-d, which renders it unique among the eight monodeuteroparaffins, C_1–C_4, permits an estimate of the upper limit of the C_3H_8 and C_3H_8-1-d contents of this substance to be made despite the absence of an authentic standard for comparison. In Fig. 6 there are shown the absorption curves of ordinary propane (Phillips' Certified Research Grade), and the samples of propane-1-d and propane-2-d in the region, 12.6–14.0 μ. The absorption band of propane at 13.4 μ is attributed to the out of plane rocking frequency of the methylene group. It will be noted that the center of this band is shifted to *ca.* 13.5 μ and the absorption is considerably weakened in the spectrum of propane-1-d, while it virtually vanishes (from this spectral region) from the spectrum of propane-2-d. If the slight absorption of the propane-2-d at 13.4 μ (2%) is assumed to be all due to the presence of propane-d_0, then the upper limit to the concentration of propane-d_0 in this sample is 2%. Similarly if the 2% absorption at 13.5 μ is attributed to propane-1-d, the upper limit to the concentration of propane-

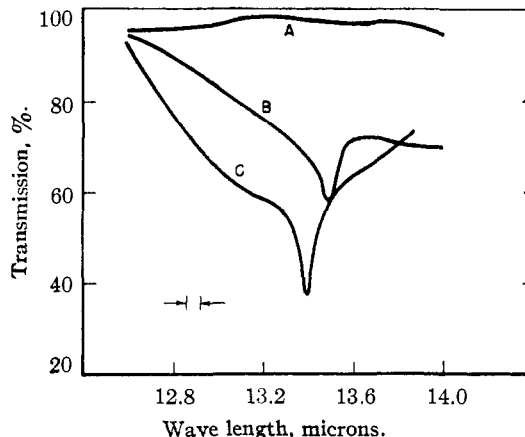(11) R. R. Brattain, *et al.*, to be published.

Fig. 6.—The infrared absorption of the isotopic propanes, propane-d_0, propane-1-d, and propane-2-d in the vicinity of the 13.4μ band, CH_2 group out of plane rocking frequency. The gas pressure is 300 mm. in a 10-cm. cell in all cases.   (A) C_3H_8-2-d, (B) C_3H_8-1-d, (C) C_3H_8.

1-d in the sample is 4%. The mass spectrometric estimate of the propane-d_0 content of the propane-2-d sample is consistent with the deduction from the absorption spectrum of the sample.

Summary

Generally applicable methods for the determination of C_nH_{2n} and C_nH_{2n+2} impurities in preparations of $C_nH_{2n+1}D$ are described. The methods, based on the properties of the initial portions of the ionization efficiency curves of ions in mass spectra, permit the detection of 0.01 to 0.05% C_nH_{2n} and 0.5–1.0% C_nH_{2n+2} in $C_nH_{2n+1}D$ for $n \geqslant 3$ even in the absence of authentic samples of $C_nH_{2n+1}D$ for comparison purposes. The mass spectrometric data necessary for performing such analyses of monodeutero-methane, -ethane, -propane and -butane preparations are given in figures.