

3-Bromo-4'-methyl-benzophenone is prepared by refluxing a toluene solution of *m*-bromo-

benzoic acid over phosphorus pentoxide.

RIVERSIDE, ILLINOIS

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO AND THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY, CHICAGO]

## Raman Spectra of the Hexanes and Heptanes<sup>1</sup>

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The study of the Raman spectra of paraffin hydrocarbons is worth while both from the standpoint of the theory of molecular structure and as a practical method for the analysis and identification of paraffins in mixtures.

For many molecules, particularly those of high degree of symmetry, a satisfactory correlation has been made of the normal modes of vibration with the observed vibrational frequencies. For the vast majority of molecules, on the contrary, no such correlation is possible at present, partly because the normal vibrations are not known and partly because the experimental data are insufficient.

Among the molecules which have not yet received adequate treatment are the chain molecules, exemplified by the paraffin hydrocarbons.<sup>2</sup> While the recent analysis of the vibrational spectrum of ethane<sup>3</sup> has provided a start in the understanding of these spectra, little in detail can be said about them until the theory has been extended to more complicated cases. It can be anticipated, however, that the paraffin isomers, which contain a small number of different kinds of bonds and differ primarily in symmetry, will furnish the best test of future theoretical developments.

From a more practical point of view, the application of these Raman spectra to the *qualitative* and *semi-quantitative analysis of hydrocarbon* mixtures is of great value because the number and chemical similarity of the hexane and heptane isomers make the purely chemical analytical methods very difficult in the case of hexanes<sup>4</sup> and practi-

cally impossible in the case of heptanes. The results obtained in the analysis of paraffin mixtures and the identification of specific isomers will be described in a separate publication.<sup>5</sup>

In this paper we present the Raman spectra of all the nine possible heptane and five possible hexane isomers. Of the heptanes only the normal compound<sup>6</sup> has been studied previously, while data for all five of the hexanes<sup>7</sup> have been reported. Since this latter work seemed quite incomplete, a repetition was thought advisable.

A study of the spectra of the eighteen isomeric octanes is in progress.

### Experimental

Exceptionally pure synthetic paraffins were available for this investigation due to the cooperation of G. Calingaert of the Ethyl Gasoline Corporation, Detroit, P. L. Cramer of the General Motors Corporation, Detroit, F. D. Rossini of the National Bureau of Standards, and J. Smittenberg of the N. V. de Bataafsche Petroleum Maatschappij, The Hague. For a sample of 2-methylpentane from natural gas we are indebted to J. H. Bruun of the Sun Oil Company.

We wish to express our thanks for the opportunity of working with these samples.

Six paraffins were available from two independent sources and one was available from three.

The sources of the individual preparations are given in Table I, in which the tube numbers marked with an asterisk refer to samples used in obtaining the spectra reported here. The indices of refraction of all samples used were determined and found to be practically identical with the best literature values (see Table I). The close agreement between the values for hydrocarbons from two or three sources is a further proof of their purity. In addition, it is important to stress the fact that the spectra of the same paraffins from different sources were identical.

The spectra were excited by four low-voltage mercury arcs. Photographs were taken with a Steinheil spectrograph whose dispersion varies from 6 Å./mm. at 4000 Å.

(1) A preliminary account of this work was presented to the Petroleum Division at the Milwaukee meeting, September, 1938. Tables V-XVIII, furnishing additional data, have been issued through Auxiliary Publication, and may be obtained from American Documentation Institute, c/o Offices of Science Service, 2101 Constitution Ave., Washington, D. C., by ordering Document 1158, remitting 24¢ for copy in microfilm, or \$1.60 for copy in photoprints legible without mechanical aid.

(2) The most ambitious theoretical attempt in this direction was that of Kassel, *J. Chem. Phys.*, **3**, 326 (1935).

(3) Crawford, Avery and Linnett, *ibid.*, **6**, 682 (1938); Schäfer, *Z. physik. Chem.*, **40**, 357 (1938).

(4) A. V. Grosse and V. N. Ipatieff, papers presented before the 94th Meeting of the American Chemical Society at Rochester, N. Y., Sept., 1937, Petroleum Division, O, p. 11.

(5) See E. J. Rosenbaum, A. V. Grosse and H. F. Jacobson, paper presented before the 96th Meeting of the American Chemical Society at Milwaukee, Wis., Sept., 1938, Petroleum Division, O, pp. 10 and 11.

(6) Most recently by Kohlrausch and Köppl, *Z. physik. Chem.*, **B26**, 209 (1934).

(7) Andant, Lambert and Lecomte, *Compt. rend.*, **198**, 1306 (1934).

TABLE I

B. = J. H. Bruun,<sup>9</sup> Sun Oil Co. Ca. = G. Calingaert, Ethyl Gasoline Corporation, Detroit. Cr. = P. L. Cramer,<sup>10</sup> General Motors Corporation, Detroit. R. = F. D. Rossini, National Bureau of Standards. Sch. = L. Schmerling,<sup>11</sup> Universal Oil Products Company, Chicago. Sm. = J. Smittenberg, N. V. de Bataafsche Petroleum Maatschappij.

Tube No.	Paraffin	$n_D^{20}$ of sample	Best literature value*	Source (see Key above)
Hexanes				
R-34*	n-Hexane	1.3752	1.3751	Cr.
R-5				
R-6	2-Methylpentane	1.3718	1.3717	Cr.
R-30*	2-Methylpentane	1.3716		
R-31	2-Methylpentane	1.3716		
R-38*	3-Methylpentane	1.3765	1.3765	R.
R-7	3-Methylpentane	1.3775		
R-33*	2,2-Dimethylbutane	1.3688	1.3690	Sch.
R-8	2,2-Dimethylbutane	1.3692		Cr.
R-32*	2,3-Dimethylbutane	1.3751	1.3751	Sch.
R-9	2,3-Dimethylbutane	1.3750		Cr.
Heptanes				
R-21*	n-Heptane	1.3878	1.3877	Sm.
R-22*	2-Methylhexane	1.3852	1.3851	Sm.
R-23*	3-Methylhexane	1.3886	1.3887	Ca.
R-24*	2,2-Dimethylpentane	1.3824	1.3823	Sm.
R-25*	2,3-Dimethylpentane	1.3920	1.3920	Sm.
R-26*	2,4-Dimethylpentane	1.3816	1.3823	Sm.
R-27*	3,3-Dimethylpentane	1.3910	1.3911	Sm.
R-18*	3,3-Dimethylpentane	1.3908		
R-28*	3-Ethylpentane	1.3936	1.3937	Ca.
R-20	2,2,3-Trimethylbutane	1.3894	1.3894	Ca.
R-29*	2,2,3-Trimethylbutane	1.3896		Sm.

to 19 Å./mm. at 5000 Å. At least two exposures were taken with each sample, one without a filter and one through sufficient sodium nitrite solution to eliminate the mercury 4047 Å. line and all lines of shorter wave length as exciting lines. An iron arc spectrum was photographed on each plate. With the Gaertner traveling microscope used to measure the position of the Raman lines, the sharper ones could be located to within 0.005 mm. Wave lengths were computed by interpolation between adjacent iron lines. The precision attained for each Raman line depends of course on the intensity, width, and diffuseness of the line. In general, the displacement values from each of the exciting lines agree within 3 cm.<sup>-1</sup>.

#### Data

In the following summaries the mercury exciting lines are designated by Kohlrausch's symbols: e 22938, i 24516, k 24705, p 27353, and q 27388 cm.<sup>-1</sup>. The values of Raman displacements excited by only one mercury line are less certain than those of other lines. The intensity on a 0-10 scale is placed after the best value for each line. Since intensities were estimated visually, they are strictly comparable only for a single compound. The symbols b and d represent broad and diffuse, respectively.

(8) See A. V. Grosse and G. Egloff, Universal Oil Products Co. Bulletin No. 219, 1938.

(9) J. H. Bruun, M. M. Hicks-Bruun and W. B. M. Faulconer, THIS JOURNAL, 59, 2355 (1937).

(10) P. L. Cramer and M. J. Mulligan, *ibid.*, 55, 374 (1936).

(11) The hexanes were fractionated on a 100-plate Bruun column. The different cuts on the plateau proved to have identical indices of refraction. Only the middle cut was used for this investigation.

**n-Heptane.**—286(0)(k,e), 310(4)(k,i,e), 355(1)(k,e), 394(1d)(e), 454(0)(k,e), 496(0)(e), 728(0)(e), 741(0)(e), 781(1)(k,e), 836(1)(k,e), 854(1)(k,e), 887(3)(k,e), 904(5d)(k,e), 936(1d)(k,e), 951(0d)(k,e), 1025(1)(k,e), 1045(3)(k,i,e), 1083(1)(k,i,e), 1139(0)(k,e), 1160(0)(k,e), 1204(1)(k), 1261(1)(k), 1303(6)(k,i,e), 1346(1)(k,e), 1364(1)(k,e), 1438(8)(k,e), 1457(8)(k,e), 2732(1)(k,e), 2851(4)(q,k,i,e), 2861(2)(k,e), 2876(4)(p,k,i,e), 2903(3)(p,k,e), 2916(1)(k,e), 2937(10)(q,p,k,i,e), 2962(8)(q,k,i,e).

**2-Methylhexane.**—306(4)(k,e), 409(2)(e), 432(2)(e), 784(3)(k,e), 821(5)(k,e), 872(4)(k,e), 893(4)(k,e), 936(2)(k,e), 956(2)(k,e), 1052(0d)(k,e), 1065(0d)(k,e), 1144(4)(k,e), 1173(3)(k,e), 1299(4)(k,e), 1336(4)(k,e), 1438(7)(k,e), 1460(7)(k,e), 2847(5)(q,k,e), 2870(10)(p,k,e), 2913(6)(q,k,i,e), 2938(7)(q,p,k,i,e), 2961(10)(q,p,k,i,e).

**3-Methylhexane.**—147(0)(e), 165(0)(k,e), 328(4)(i,e), 337(1d)(e), 381(1)(k,e), 428(3)(k,e), 449(3)(k,e), 556? (0)(k,e), 735(1d)(k,e), 761(1)(k,e), 772(3)(k,i,e), 798(1)(e), 821(4)(k,i,e), 846(1)(e), 864(1)(k,e), 882(3)(k,i,e), 931(5d)(k,e), 984(5d)(k,i,e), 1034(6)(k,i,e), 1051(5)(k,e), 1150(2)(k,e), 1173(4d)(k,e), 1299(4d)(k,e), 1340(1d)(k,e), 1356(1d)(k,e), 1382(3d)(k,e), 1446(7)(k,e), 1463(7)(k,e), 2735(1)(k,e), 2848(1)(q,k,e), 2858(7)(k,i,e), 2878(10)(p,k,i,e), 2914(7)(q,k,i,e), 2940(9)(q,k,i,e), 2966(8)(q,p,k,i,e).

**3-Ethylpentane.**—307(1)(e), 351(1)(k), 397(2)(k,e), 441(2d)(k,e), 452(0)(k,e), 551(0)(e), 732(5)(k,e), 829(2)(k,e), 843(1d)(k,e), 897(2)(e), 904(2)(k,e), 1000(3d)(k,e), 1038(1)(k,e), 1053(0)(k,e), 1166(1)(k,e), 1447(5)(k,e), 1463(4)(k,e), 2823(2)(k,i,e), 2856(8)(k,i,e), 2878(10)(p,k,i,e), 2911(7)(q,k,e), 2935(10)(q,p,k,i,e), 2965(8)(q,p,k,i,e).

**2,2-Dimethylpentane.**—320(3)(k,e), 338(1)(e), 345(4)(k,e), 426(1)(e), 493(4)(k,e), 746(10)(k,e), 881(5)(k,e), 928(6)(k,e), 1043(3)(k,e), 1098(1)(k,e), 1208(3)(k,e), 1247(2)(k,e), 1267(1)(k,e), 1316(1)(k,e), 1447(7)(k,e), 1466(5)(k,e), 2712(2)(k,e), 2781(2)(k,e), 2845(2)(k,i,e), 2866(2d)(k,e), 2875(4)(p,k,i,e), 2885(3)(k,e), 2909(10)(q,p,k,i,e), 2935(4d)(q,p,k,i,e) (double?), 2961(10)(k,i,e).

**2,3-Dimethylpentane.**—352(0)(k), 380? (0d)(k), 431(2)(k,e), 462(2)(k,e), 481(1)(k,e), 498(2)(k,e), 552(0)(k,e), 712(4)(k,i,e), 740(5)(k,e), 752(5)(k,e), 786(1)(k,e), 799(0)(k,e), 850(2)(k,e), 916(3)(k,e), 955(2)(k,e), 968(2)(k,e), 983(2)(k,e), 996(0)(k), 1013(1)(k,e), 1038(0)(k,e), 1105(0)(k), 1168(1)(k,e), 1189(2)(k,e), 1238(0)(k), 1285(3)(k,e), 1311(0)(k,e), 1351(1)(k,e), 1444(7)(k,e), 1463(7)(k,e), 2782? (1)(k,e), 2862(6)(p,k,i,e), 2876(10)(p,k,i,e), 2898(4)(q,k,i,e), 2908(4)(q,p,k,i,e), 2937(8)(q,p,k,i,e), 2966(10)(q,p,k,i,e).

**2,4-Dimethylpentane.**—137(2)(k,e), 308(6)(k,e), 336(0)(k), 353(1d)(k,e), 380(1)(k), 419(1d)(k,e), 469(5)(k,i,e), 497(0)(k), 687(1)(k,e), 714(1)(k,e), 728(2)(k,e), 807(10)(k,e), 871(2)(k,e), 918(5)(k,e), 925(1)(k,e), 985(2)(k,e), 996(3)(k,e), 1037(3)(k,e), 1077(2)(k,e), 1109(0d)(k,e), 1157(5)(k,e), 1173(5)(k,e), 1250(3)(k,i,e), 1300(0)(k), 1320(7)(k,i,e), 1347(7)(k,i,e), 1449(7)(k,e), 1467(7)(k,e), 2759(4)(q,p,k,e), 2841(5)(q,k,i,e), 2871(10b)(p,k,i,e), 2916(4)(q,k,e), 2936(4)(q,p,k,e), 2968(10b)(q,k,i,e).

**3,3-Dimethylpentane.**—294(1)(e), 312? (1d)(k), 352(1)(k,e), 375(2)(k,e), 384(1)(k), 412(3)(k,e), 445(4)(k,e), 486(3)(k,e), 513(1)(k,e), 694(10)(k,e), 707(3)(k,e), 854(4)(k,e), 897(1)(k,e), 913(5)(k,e), 934(4)(k,e), 986(3)(k,e), 1002(3d)(k,e), 1007(3d)(k), 1016(0)(k,e), 1037(4)(k,e), 1080(6d)(k,e), 1196(3)(k,i,e), 1218(1)(k,e), 1239(3)(k,e),

1287(2)(k,e), 1316(2)(k,e), 1339(3)(k,e), 1394(2)(k,e), 1446(8)(k,e), 1468(6)(k,e), 2716(1)(k,e), 2739(2)(k,e), 2858(4)(q,k,e), 2868(4)(p,k,i,e), 2891(9)(p,k,i,e), 2908(9)(p,k,e), 2944(10)(q,p,k,i,e), 2969(10)(q,p,k,i,e).

**2,2,3-Trimethylbutane.**—299(1)(k,e), 363(2)(k,e), 391(3)(k,e), 444(1)(k,e), 460(1)(k,e), 524(4)(k,e), 689(10)(k,i,e), 833(1)(k,e), 919(3d)(k,i,e), 926(3)(k,e), 957(0)(k,e), 1027(5)(k,i,e), 1084(4)(k,e), 1105(2)(k,e), 1159(0)(k,e), 1253(2d)(k,e), 1320(0)(k,e), 1333(0)(k,e), 1454(5)(k,e), 1473(5)(k,e), 2716(1)(k,i,e), 2758(1)(q,p,k,i), 2872(10)(p,k,i,e), 2909(10)(q,k,i,e), 2928(1)(k,e), 2947(6d)(q,p,k,e), 2965(6d)(q,p,k,e), 2979(6d)(q,k,e).

**n-Hexane.**—313(1)(k,e), 332(1)(e), 371(4)(i?, =e), 401(3)(=e), 455?(0)(e), 809?(0)(e), 824(3)(k,e), 870(3)(k,e), 892(4)(k,i,e), 899(4)(k,e), 953(0)(i?,e), 974(0)(e), 1005(0)(e), 1040(3)(k,e), 1080(3)(k,e), 1139?(1)(k,e), 1305(4)(k,e), 1438(6)(k,e), 1460(6)(k,e), 2733(1)(k,e), 2853(7)(k,i,e), 2865(7)(p,k,i,e), 2877(10)(p,k,i,e), 2902(3)(q,p,k,e), 2921(3)(k,i,e), 2940(10)(q,p,k,i,e), 2964(8)(q,p,k,i,e).

**2-Methylpentane.**—322(3)(k, =e), 381(0)(k,e), 395(0)(e), 446(3)(k, =e), 734(1)(k,e), 782(1)(k,e), 814(6)(k,e), 857(1)(k,e), 890(1)(k,e), 955(3)(k,e), 1037(3)(k,e), 1070(1)(k,e), 1147(2)(k,e), 1171(1)(k,e), 1240(1)(e), 1298(3)(k,e), 1338(3)(k,e), 1444(6)(k,e), 1462(6)(k,e), 2847(4)(q,p,k,i,e), 2871(10b)(p,k,i,e), 2915(6)(k,i,e), 2934(6)(q,p,k,i,e), 2962(8b)(p,k,i,e).

**3-Methylpentane.**—387(1)(k,e), 445(6)(k, =e), 470?(0)(e), 736(2)(k,e), 748(4)(k,e), 754(4)(k,e), 767(2)(k,e), 817(5)(k,e), 879(2d)(k,e), 966(2d)(e), 988(2d)(e), 1018(2)(k,e), 1038(4)(k,e), 1050(4)(k,e), 1157(1d)(k,e), 1174(1d)(k,e), 1278(2d)(k,e), 1354(2)(k,e), 1379(0)(k,e?), 1447(7)(k,e), 1460(7)(k,e), 2856(10)(q,k,i,e), 2878(10)(p,k,i,e), 2899(3)(p,k,i,e), 2913(3)(q,k,i,e), 2937(9)(q,p,k,i,e), 2964(9)(p,k,i,e).

**2,2-Dimethylbutane.**—259(1)(k,e), 335(0)(e), 361(1)(k,e), 485(1)(k,e), 711(10b)(k,i,e), 869(3)(k,e), 927(3b)(k,e), 1017(2b)(k,e), 1075(2)(k,e), 1217(3d)(k,e), 1251(2b)(k,e), 1304(1d)(k,e), 1448(6d)(k,e), 1467(4d)(k,e), 2713(2)(p,k,e?), 2782(1)(q,k,e), 2856(2)(p,k,e), 2871(5)(p,k,e), 2890(3)(q,k,e), 2906(10)(q,p,k,i,e), 2942(6d)(q,k,i,e), 2967(6d)(q,p,k,i,e).

**2,3-Dimethylbutane.**—291(0)(e), 346(0)(e), 479(3)(k,e), 505(3)(k,i, =e), 728(8)(k,i,e), 756(6)(k,e), 869(1b)(k,e), 932(3)(k,e), 942(3)(k,e), 955(1)(k,e), 1033(2b)(k,e), 1161(2b)(k,i,e), 1198(2b)(k,e), 1299(1b)(k,e), 1346(2b)(k,e), 1447(6)(k,e), 1468(6)(k,e), 2720(1)(k,e), 2760(1)(k,e), 2860(3)(k,e), 2874(10)(p,k,i,e), 2903(3d)(q,p,k,i,e), 2936(3d)(q,p,k,e), 2965(6d)(q,p,k,i,e), 2980(3d)(k,e).

### Discussion

In Table II the data presented here for *n*-hexane and *n*-heptane are compared with the results of Kohlrausch and Köppl.<sup>6</sup> It can be seen that, except for some of the weaker lines, the concordance is quite satisfactory. No comparison is made with the hexane spectra reported by Andant, Lambert and Lecomte,<sup>7</sup> as the discrepancies seem to be beyond experimental error.

All of the spectra reported here show the characteristic features associated with the presence of

TABLE II

<i>n</i> -HEXANE			
K. and K.	R., G. and J.	K. and K.	R., G. and J.
318(2b)	313(1)	1034(3)	1040(3)
	332(1)	1075(3b)	1080(3)
365(3)	371(4)	1134(1)	1139?(1)
398(1)	401(3)	1167?(0)	
	455?(0)	1301(5b)	1305(4)
728(1/2)		1441(4)	1438(6)
	809?(0)	1453(6b)	1460(6)
820(5b)	824(3)	2724(4)	2733(1)
865(3)	870(3)	2851(10)	2853(7)
894(6)	892(4)	892(4)	2865(7)
	899(4)	2874(12)	2877(10)
	953(0)	2908(10)	2902(3)
966(00)			2921(3)
	974(0)	2935(11)	2940(10)
1006(1)	1005(0)	2962(8)	2964(8)
<i>n</i> -HEPTANE			
	286(0)	1134(2b)	1139(0)
309(5)	310(4)	1160(0)	1160(0)
	355(1)		1204(1)
394(2b)	394(1d)		1261(1)
	454(0)	1301(6b)	1303(6)
490(0)	496(0)	1359(0)	1346(1)
736(0)	728(0)		1364(1)
	741(0)	1439(5)	1438(8)
774(1b)	781(1)	1459(6)	1457(8)
836(3)	836(1)	2720(3vb)	2732(1)
	854(1)	2853(12)	2851(4)
	887(3)		2861(2)
900(4)	904(5d)	2874(12)	2876(4)
938(0)	936(1d)	2902(12)	2903(3)
	951(0d)		2916(1)
1013(1)	1025(1)	2933(12)	2937(10)
1046(2)	1045(3)	2962(9)	2962(8)
1073(3b)	1083(1)		

C-H bonds in the molecules: strong lines on a continuous background in the region 2800–3000 cm.<sup>-1</sup> and two broad and fairly strong lines near 1450 cm.<sup>-1</sup>. These portions of the spectrum show relatively little change, either with the number or the arrangement of carbon atoms in the molecule. In marked contrast, the lines of lower frequency, which are attributed to the valence and deformation vibrations of the carbon skeleton, show a great variation in passing from one isomer to another.

In some cases a slight similarity was noticed in the spectra of compounds of closely related structures. For example, there seems to be more than an accidental number of coincidences in the spectra of 2,2-dimethylbutane and 3,3-dimethylpentane, and these have a resemblance to the spectrum of tetramethylmethane. 2-Methylpentane, 3-methylhexane and 2-methylhexane have some features in common. On the other hand, the

spectra of 3-ethylpentane and 3-methylpentane are surprisingly different.

We wish to thank the Physics Department for the use of a traveling microscope.

### Summary

The Raman spectra of the five hexanes and the nine heptanes are described.

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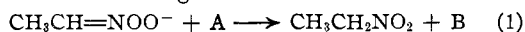
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

## Kinetics of Isomerization of Aci to Nitro Forms of Nitroethane in H<sub>2</sub>O and D<sub>2</sub>O

BY SAMUEL H. MARON<sup>1</sup> AND VICTOR K. LA MER

In a preceding paper<sup>2</sup> were reported kinetic studies in H<sub>2</sub>O and D<sub>2</sub>O on the isomerization of nitro- to aci-nitroparaffins in presence of hydroxyl and deuterioxy ions. In this paper are described kinetic measurements of the reverse process, namely, the conversion of aci-nitroethane to nitro-nitroethane in presence of H<sub>3</sub>O<sup>+</sup> in H<sub>2</sub>O at 0 and 5°, and in presence of D<sub>3</sub>O<sup>+</sup> in D<sub>2</sub>O at 5°.

The kinetics and mechanism of regeneration of nitroethane from the aci form were first studied quantitatively by Junell<sup>3</sup> in various buffer mixtures in H<sub>2</sub>O at 0°. He showed that the reaction proceeds according to the scheme



where A and B are acids and bases in general, as defined by Brönsted.<sup>4</sup> The specific rate constants for the various acids used obey the Brönsted relation between catalytic constant and acid strength,

$$\frac{k_A}{p} = G \left( \frac{q}{p} K_A \right)^\alpha$$

The rate constant for the isomerization in presence of H<sub>3</sub>O<sup>+</sup> was not measured directly, but was inferred from the kinetics of the reaction in buffered solutions in which the hydrogen ion concentration was appreciable. The course of the reaction was followed by bromination of the aci-nitroethane.

Because of certain discrepancies observed between the results of the bromination and conductance methods,<sup>2</sup> and because of the indirect nature of Junell's result for H<sub>3</sub>O<sup>+</sup>, it was deemed desirable to investigate directly the reaction with H<sub>3</sub>O<sup>+</sup> at 0° by conductance, and to extend the measurements to 5° and to D<sub>2</sub>O as solvent.

### Experimental

The chemicals, apparatus, and general procedure

(1) Present address: Department of Chemical Engineering, Case School of Applied Science, Cleveland, Ohio.

(2) Maron and La Mer, *THIS JOURNAL*, **60**, 2588-2596 (1938).

(3) Junell (a) *Arkiv Kemi, Mineral. Geol.*, **11B**, No. 30 (1934); (b) *Svensk Kem. Tid.*, **46**, 125-136 (1934); (c) Dissertation, University of Uppsala, Sweden, 1935, pp. 99-110.

(4) Brönsted, *Chem. Rev.*, **5**, 231 (1928).

have been described.<sup>2</sup> The reaction was initiated by adding to barium nitroethane in a conductivity cell an equivalent quantity of H<sub>2</sub>SO<sub>4</sub> (in H<sub>2</sub>O) or D<sub>2</sub>SO<sub>4</sub> (in D<sub>2</sub>O). The rate of isomerization of the liberated acid of aci-nitroethane was followed by measuring the variation of resistance of the solutions with time.

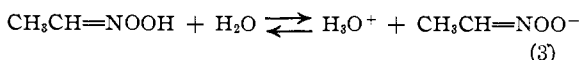
A relation between resistances observed and the rate constants can be obtained as follows. Let:

- $a$  = total initial concentration of aci-nitroethane
- $(a - x)$  = total concentration of aci-nitroethane at time  $t$
- $(\text{N}^-)$  = concentration in equivalents per liter of the anion of aci-nitroethane at time  $t$
- $(\text{HN})$  = concentration of un-ionized aci-nitroethane at time  $t$
- $K_H$  = Ionization constant of  $\text{CH}_3\text{CH} = \text{NOOH}$

Then

$$(\text{HN}) + (\text{N}^-) = (a - x) \quad (2)$$

Since the equilibrium



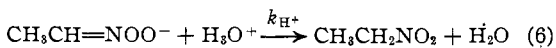
is always maintained

$$K_H = \frac{(\text{H}_3\text{O}^+)(\text{N}^-)}{(\text{HN})} \quad (4)$$

where  $K_H$  is expressed in terms of concentrations rather than activities. At the low ionic strengths used in the experiments described here, this assumption introduces no serious error. Eliminating  $(\text{HN})$  between (2) and (4), it follows that

$$(\text{N}^-) = \frac{(a - x)K_H}{(\text{H}_3\text{O}^+) + K_H} \quad (5)$$

From Junell's work<sup>3</sup> it may be expected that the isomerization with H<sub>3</sub>O<sup>+</sup> should proceed according to



and with the rate equation

$$\begin{aligned} \frac{-d(a - x)}{dt} &= k_{H^+}(\text{N}^-)(\text{H}_3\text{O}^+) \\ &= k_{H^+}(\text{N}^-)^2 \end{aligned} \quad (7)$$

since  $(\text{N}^-) = (\text{H}_3\text{O}^+)$  in the experiments in ques-