The Isomerization of Propane with C13 in One End Position

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TABLE I. Apparent percentage of exchange. Solutions 0.011 molar in cobaltic and cobaltous cobalt.

Solutions	Time in hours	Apparent percent exchange
1 M HCl	3.5	0.03 ±0.05
neutral	3.5	0.02 ±0.07
neutral	24	0.03 ±0.07
3.6 M NH$_3$	3.5	0.19 ±0.24
6.5 M NH$_3$	3.5	0.05 ±0.13
6.0 M NH$_3$	24	0.03 ±0.25
9.5 M NH$_3$	3.5	0.02 ±0.07

of the complex and an equimolar quantity of inactive cobaltous chloride was dissolved in water and hydrochloric acid or ammonia water added to give the desired solution. After standing in the dark for a known time at room temperature, the solution was neutralized, ammonium chloride and ammonium thiocyanate added and the complex cobaltous thiocyanate extracted with amyl alcohol-ether mixture. The cobalt was removed from the organic layer by shaking with a dilute ammonia solution and then precipitated by the addition of ammonium sulfide. The cobalt sulfide was dissolved in aqua regia and the resulting solution boiled with sulfuric acid. The cobalt was deposited electrolytically on weighed copper disks and the radioactivity determined. Radioactivity measurements were made with a mica window end-on type of counter with a scale of 64 circuit.

All experiments were done in duplicate. Corrections were made for background and for the incomplete recovery of the cobaltous cobalt. Blank experiments indicated that less than 0.1 percent of the hexammino cobaltic ion was extracted under the conditions of these experiments.

The results are given in Table I. The initial activity of the hexammino cobaltic ion taken for each of the different experiments varied between 2400 and 3000 counts a minute. The results are reported as the apparent percentage of the hexammino cobaltic chloride undergoing exchange with all of the divalent cobalt present. The uncertainties were calculated taking the statistical error in the determination of the background and cobalt activity as the square root of the number of counts observed.

In all cases the apparent percent exchange is zero within experimental error. The results in neutral solution confirm those of Flagg. However, his suggestion that the non-exchange is due to the rapid reduction of the cobaltic ion by water is not by itself sufficient to account for these results. In his experiments the activity was present in the cobaltous state while in those reported here the hexammino cobaltic ion contained the activity. Dissociation of the complex by reaction (1) and reduction of the cobaltic to cobaltous ion would result, in these experiments, in activity being detected when the cobaltous ion was separated. Ascribing the total activity in the cobaltous state to such decomposition (as well as the results of additional blank experiments) indicates that less than 0.1 percent of the complex was decomposed in solution in twenty-four hours. Thus, either the dissociation of the complex to form cobaltic ions, the reduction of cobaltic ion, or both, must be slow processes.

The lack of exchange in strongly ammoniacal solution indicates that if, as Lamb and Larson conclude,[2] divalent cobalt exists as the $Co(NH_3)_6{}^{2+}$ ion under these conditions, exchange between the latter and $Co(NH_3)_6{}^{3+}$ does not occur by an electron transfer between the complex ions under the conditions of these experiments. Further experiments on the exchange reactions of the cobaltammines are in progress and will be reported elsewhere.

We wish to acknowledge the generous financial assistance of the National Research Council of Canada.

[1] J. F. Flagg, J. Am. Chem. Soc. 63, 557 (1941).
[2] A. B. Lamb and A. T. Larson, J. Am. Chem. Soc. 42, 2024 (1920).
[3] Biltz, Hall, and Blanchard, *Laboratory Methods of Inorganic Chemistry* (John Wiley and Sons, Inc., New York, 1928).
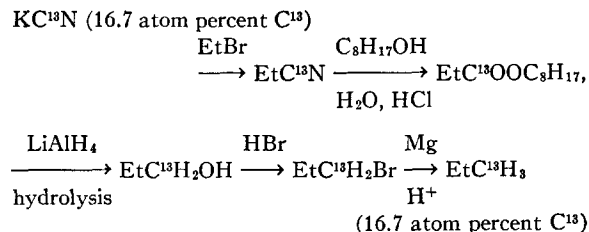
The Isomerization of Propane with C13 in One End Position

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THE catalytic isomerization of propane with C13 in one end position, for which the nomenclature propane-1-C13 has been suggested,[1] was investigated over aluminum bromide at room temperature. It was found that the rate of isomerization of propane-1-C13 to propane-2-C13 with C13 in the middle position is comparable to the rate of isomerization of normal butane to isobutane under similar conditions. Within the accuracy of the analytical method the equilibrium distribution of the propanes-1-C13 and -2-C13 was found to be the statistical one, that is propane-1-C13/propane-2-C13 = 2, as would be expected since the introduction of C13 into the propane molecule changes the partition functions only very slightly. The result that no molecules containing two C13 carbon atoms are formed, unambiguously establishes the purely intramolecular character of the isomerization reaction. Finally, it was found that the probability for dissociation by electron impact in the mass spectrometer of the carbon − carbon bonds was decreased by roughly 5 percent for the C13 − C12 bond and increased by the same amount for the C12 − C12 bond below and over those in ordinary propane.*

Propane-1-C13 prepared through the reaction sequence:

KC13N (16.7 atom percent C13)

$$\xrightarrow{\text{EtBr}} EtC^{13}N \xrightarrow[H_2O, HCl]{C_8H_{17}OH} EtC^{13}OOC_8H_{17},$$

$$\xrightarrow[\substack{\text{hydrolysis}}]{LiAlH_4} EtC^{13}H_2OH \xrightarrow{HBr} EtC^{13}H_2Br \xrightarrow[H^+]{Mg} EtC^{13}H_3$$

(16.7 atom percent C13)

gives in 30 percent yield a propane with the calculated isotopic and isomeric distribution shown in column 2 of Table I. The mass spectrometric technique used combines into one operation the usual steps of chemical degradation followed by isotopic analysis.

The relative concentrations of the four isotopic propanes can be calculated by well-known methods from the relative intensities of the ions of $m/q = 47^+$, 46^+, 45^+, and 44^+ in the mass spectrum of a sample, when the relative intensities

TABLE I. Calculated distribution of isotopic species of C^{13}(16.7 percent)-propane.

Species	Propane synthesized	After intramolecular equilibration	After intra- plus intermolecular equilibration
$C_3^{12}H_8$	0.8150	0.8150	0.8237
$C^{12}H_3-C^{12}H_2-C^{13}H_3$	0.1720	0.1204	0.1100
$C^{12}H_3-C^{13}H_2-C^{12}H_3$	0.00856	0.0602	0.0550
$C^{13}H_3-C^{13}H_2-C^{12}H_3$	0.00182	0.00236	0.00734
$C^{13}H_3-C^{12}H_2-C^{13}H_3$	0.00172	0.00118	0.00367
$C_3^{13}H_8$	0.00002	0.00002	0.00025
$(46^+)/(44^+)\pm0.0003$[a]	0.0037	0.0037	0.0118
$(30^+)/(29^+)\pm0.0010$[a]	0.1020[b]	0.1300[b]	0.1265[b]

[a] Accuracy of measurement of these quantities.
[b] Calculated assuming equal dissociation probability for $C^{12}-C^{12}$ and $C^{12}-C^{13}$ bonds.

TABLE II. Mass spectral relative intensities in C^{13}-propane during isomerization.

Time[a]	$(30^+)/(29^+)$	$(46^+)/(44^+)$
0[b]	0.106(3)	0.0038
65	0.119(4)	0.0034
186	0.126(5)	0.0034
261	0.128(3)	0.0036
405	0.130(1)	0.0039
594	0.129(5)	0.0036
1074	0.133(6)	0.0039

[a] Time in hours of contact between vapor at approximately 450-mm pressure with a catalyst prepared by the addition of 0.023-gram H_2O to anhydrous aluminum bromide (0.40 gram).
[b] The propane-1-C^{13} as synthesized. The intensities of all of the C_2 and C_3 ions and ionic fragments agreed with the calculated values to within the experimental uncertainty.

of the ions of $m/q=44^+$, 43^+, 42^+, and 41^+ in the mass spectrum of $C_3^{12}H_8$ are known. Furthermore, the relative concentrations of the isomeric propanes, -1-C^{13} and -2-C^{13}, can be determined from the relative intensities of the ions of $m/q=30^+$ and 29^+ since the former species can give rise to but half as many ions $C^{12}C^{13}H_5^+(m/q=30^+)$ as can the latter species. This determination of the isotopic isomer distribution presupposes the knowledge of the concentrations of $C_3^{12}H_8$, $C_2^{12}C^{13}H_8$, $C^{12}C_2^{13}H_8$, and $C_3^{13}H_8$. Intramolecular equilibration requires the species distribution (statistical) shown in column 3 of Table I, while complete inter and intramolecular equilibration (statistical) requires the distribution shown in column 4. The relative ion intensities $(46^+)/(44^+)$ and $(30^+)/(29^+)$, which are measures of the relative species concentrations $C^{12}C_2^{13}H_8/C_3^{12}H_8$ and $C^{12}H_3-C^{13}H_2-C^{12}H_3/C^{12}H_3-C^{12}H_2-C^{13}H_3$, respectively, calculated from the mass spectrum of ordinary propane for the three situations, are shown in the last two rows of Table I.

In Table II there are shown the measured values of the relative intensities $(46^+)/(44^+)$ and $(30^+)/(29^+)$ for the prepared propane-1-C^{13} and after 65, 186, 261, 405, 594, and 1074 hours in contact with almost anhydrous aluminum bromide at 25°C. At 65 hours the $(30^+)/(29^+)$ ratio had undergone about one-half its maximum change, while even at 1074 hours the $(46^+)/(44^+)$ ratio was still unchanged (within the experimental error). The disagreement between the initial and final values in Table II and those given in Table I are believed to be due to a small ($\sim$5 percent) difference in the dissociation probabilities of $C^{12}-C^{12}$

and $C^{12}-C^{13}$ bonds. Similar experiments with butane are now in progress.

[1] J. W. Otvos and C. D. Wagner, Science 106, 409 (1947).
* Recent measurements with a sample containing 54 atom percent C^{13} allow a more exact evaluation of the changes in these dissociation probabilities, with the result that the dissociation probability of the $C^{13}-C^{12}$ bond is decreased by 12 percent±1 percent and that of the $C^{12}-C^{12}$ bond increased by 7 percent±0.2 percent.

A Criterion for Normal Liquids

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IN a recent communication Parashad[1] has proposed a formula to distinguish between normal liquids and associated liquids. For liquids which we may regard as normal, he finds

$$\Delta E^v \beta / V\alpha = T, \tag{1}$$

while for abnormal liquids, the left-hand member is greater than T

$$\Delta E^v \beta / V\alpha > T. \tag{2}$$

ΔE^v is the energy of vaporization, β is the isothermal compressibility, V is the molal volume, α is the coefficient of cubical expansion, and T is the absolute temperature.

In reality, the criterion which Parshad proposed is not novel. Pure thermodynamics yields what has been called the "thermodynamic equation of state"

$$(\partial E/\partial V)_T = T(\partial P/\partial T)_v - P. \tag{3}$$

Since for liquids under normal conditions, P is negligibly small compared with the other two terms, we may write

$$(\partial E/\partial V)_T = T(\partial P/\partial T)_v. \tag{4}$$

Since $(\partial P/\partial T)_v = \alpha/\beta$, we obtain

$$(\partial E/\partial V)_T = T\alpha/\beta.$$

It remains for us to relate $(\partial E/\partial V)_T$ and $\Delta E^v/V$. Over a small range of volumes, we may represent E and $(\partial E/\partial V)_T$ in the functional forms:

$$E = a/V^n, \tag{6}$$
$$\partial E/\partial V = -na/V^{n+1} = -nE/V. \tag{7}$$

For most practical purposes the cohesive energy per mole E may be replaced by $-\Delta E^v$, and Eq. 5 may be rewritten

$$T\alpha/\beta = n\Delta E^v/V. \tag{8}$$

For a van der Waals liquid n is unity, and this last Eq. 8 reduces to the first. Although the van der Waals equation is certainly a poor approximation for liquids, Hildebrand and co-workers have measured $(\partial P/\partial T)v$ directly for a number of normal liquids and on comparison with $\Delta E^v/V$, it was found that n is, in fact, not far from unity.[2] For methyl alcohol and mercury, although for different reasons, the calculated n falls far short of unity, in agreement with Eq. (2).

[1] R. Parshad, J. Chem. Phys. 15, 761 (1947).
[2] J. H. Hildebrand, Phys. Rev. 34, 984 (1929); see also J. H. Hildebrand, Solubility of Non-Electrolytes (Reinhold Publishing Corporation, New York, 1936), second edition, pp. 93–101, and J. Chem. Phys. 15, 727 (1947), particularly Table VII.