Ionic Reactions Occurring in Sulfuric Acid. IV.
Tritium Exchange between Tritiated Sulfuric Acid and Isoparaffins

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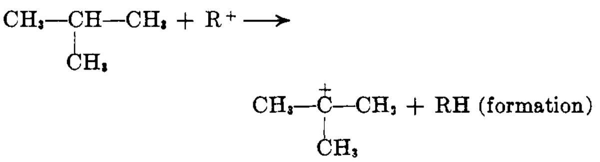
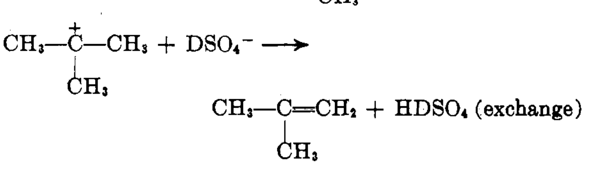
Rates of tritium exchange have been measured between tritiated sulfuric acid (H_2SO_4-H^3) and a series of isoparaffins. These exchange rates may be used as criteria for relative ease of carbonium ion formation, and it has been found that the ease of forming a carbonium ion decreases with increasing isoparaffin molecular weight. When skeletal isomerization is possible, such isomerization occurs to give products that approach thermodynamic equilibrium among hydrocarbons with the same extent of chain branching. These data may be rationalized by a picture predicated on rapid rearrangement and exchange during the lifetime of the carbonium ion.

Recent work at this laboratory[1,2] has been directed toward elucidating the mechanism of formation of pentanes, hexanes, heptanes, nonanes, and higher saturated paraffins during the course of sulfuric acid catalyzed alkylation of isobutane with butylenes. The previous research has been carried out by studying product distribution upon starting with tagged reactants. Such a study, while informative in terms of over-all reaction paths, does not provide insight into the specific reactions of the various ionic species. Such information is of vital importance since it provides data concerning the reactivities of the various postulated ionic intermediates.

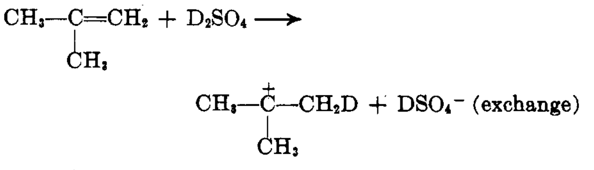
In order to obtain information on reactivity of the various ions an approach was taken that utilized tritiated sulfuric acid (H_2SO_4-H^3). Rates of tritium–protium exchange were measured between H_2SO_4-H^3 and a series of isoparaffins. Similar exchange reactions utilizing deuterium have been carried out in the past.[3-5] Beeck and co-workers[3,4] demonstrated that the exchange reaction involves all hydrogens contiguous to the ionic center, and that exchange (reactions 2a and 2b) is rapid compared to hydride transfer (reactions 1 and 3). While such deuterium tracing studies obviously provide very valuable information, measurement of tritium exchange between H_2SO_4-H^3 and a saturated paraffin could be of even greater value. This is particularly true when employed in conjunction with the radioassaying gas chromatograph.[2,6]



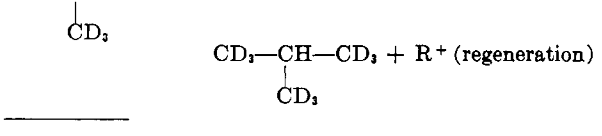
$$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_3 + R^+ \longrightarrow CH_3-\underset{CH_3}{\underset{|}{\overset{+}{C}}}-CH_3 + RH \text{ (formation)} \quad (1)$$



$$CH_3-\underset{CH_3}{\underset{|}{\overset{+}{C}}}-CH_3 + DSO_4^- \longrightarrow CH_3-\underset{CH_3}{\underset{|}{C}}{=}CH_2 + HDSO_4 \text{ (exchange)} \quad (2a)$$

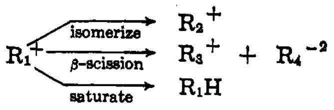


$$CH_3-\underset{CH_3}{\underset{|}{C}}{=}CH_2 + D_2SO_4 \longrightarrow CH_3-\underset{CH_3}{\underset{|}{\overset{+}{C}}}-CH_2D + DSO_4^- \text{ (exchange)} \quad (2b)$$



$$CD_3-\underset{CD_3}{\underset{|}{\overset{+}{C}}}-CD_3 + RH \longrightarrow CD_3-\underset{CD_3}{\underset{|}{CH}}-CD_3 + R^+ \text{ (regeneration)} \quad (3)$$

A prime example of the potential utility of the tritium tracing technique as employed by these studies on the fate of carbonium ion is the following. Consider an ion R_1^+ that may undergo these transformations: (a) R_1^+ may isomerize to R_2^+ (eq. 4); (b) R_1^+ may undergo β-scission (eq. 5); or (c) R_1^+ might take part in a hydride transfer reaction (eq. 6). Classical techniques could be employed to measure the first two as long as conversions were high enough. Deuterium tracing could measure all three, but again conversions would have to be rather high, particularly in measuring the amount of ion that returns to the initial hydrocarbon. Tritium tracing measures all three and conversion levels are limited only by the specific activity of the acid charge. (It will be seen that total conversions of less than 0.1% can readily be measuring by using moderately active acid.)



$$R_1^+ \xrightarrow{\text{isomerize}} R_2^+ \quad (4)$$

$$R_1^+ \xrightarrow{\beta\text{-scission}} R_3^+ + R_4^{-2} \quad (5)$$

$$R_1^+ \xrightarrow{\text{saturate}} R_1H \quad (6)$$

The results of this study, coupled with those in the succeeding paper covering the specific case of 2,2,4-trimethylpentane, provides a fairly complete picture of the primary reactions of saturated hydrocarbon carbonium ions.

Results

This study was carried out by making a series of runs, each of which used an equal volume mixture of three hydrocarbons and methylcyclopentane. Individual compositions for each experiment were arranged so that each hydrocarbon would be run twice and that possible reaction products would not interfere with hydrocarbons already present. Methylcyclopentane was employed to suppress side reactions and provide an internal standard for comparison of specific activities.

The summary of specific activities relative to that of methylcyclopentane is shown in Table I. Column three indicates any by-products formed during the reaction. (The relative specific activities listed in the second column include the activity incorporated by the starting hydrocarbon as well as that incorporated in

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[1] J. E. Hofmann and A. Schriesheim, *J. Am. Chem. Soc.*, **84**, 953 (1962).

[2] J. E. Hofmann and A. Schriesheim, *ibid.*, **84**, 957 (1962).

[3] J. W. Otvos, D. P. Stevenson, C. D. Wagner, and O. Beeck, *ibid.*, **73**, 5741 (1951).

[4] D. P. Stevenson, C. D. Wagner, O. Beeck, and J. W. Otvos, *ibid.*, **74**, 3269 (1952).

[5] G. S. Gordon and R. L. Burwell, Jr., *ibid.* **71**, 2355 (1949).

[6] A. Y. Mottlau, *Anal. Chem.*, **33**, 293 (1961).

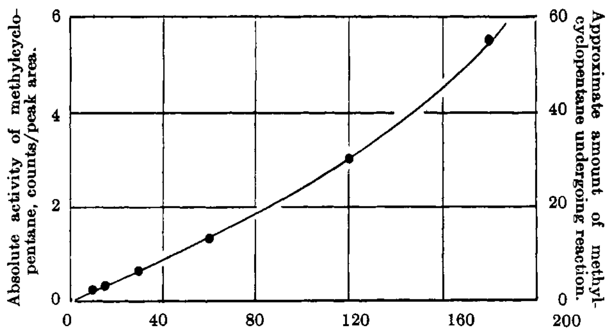


Fig. 1.—Exchange reaction exhibits autocatalytic behavior.

TABLE I

RATES OF EXCHANGE RELATIVE TO METHYLCYCLOPENTANE

	Relative rate[a]	Other compd. formed[b]
Isopentane	0.37	None
2,2-Dimethylbutane	0.0	None
2,3-Dimethylbutane	0.22	None
2-Methylpentane	0.16	3-MeC_5
3-Methylpentane	0.16	2-MeC_5
2,2,3-Trimethylbutane	0.04	None
2,3-Dimethylpentane	0.11	2,4-$DiMeC_5$
2,4-Dimethylpentane	0.065	2,3-$DiMeC_5$
3-Methylhexane	0.055	2-MeC_6
2,2,4-Trimethylpentane	0.035	*c*
2,4 + 2,5-dimethylhexane	0.075	2,3-$DiMeC_6$
2,2,5-Trimethylhexane	0.026	*d*

[a] Uncorrected for any statistical factors. Includes activity of any products formed. [b] C_5 = pentane, C_6 = hexane. [c] A number of products are formed. This will be covered in detail in the succeeding paper. [d] No by-products were measured. However, at this low conversion level, other isomers may have formed which were not detected.

any products.) Figure 1 shows the absolute rate of tritium incorporation into the methylcyclopentane for one typical experiment and indicates that the reaction is autocatalytic. This phenomenon is undoubtedly due to a gradual buildup of carbonium ion initiators *via* cracking and oxidation reactions. For this reason and the fact that traces of carbonium ion precursors, such as olefins, greatly accelerate reaction rates, run to run reproducibility in terms of absolute activity was rather poor. However, when the specific activity of each hydrocarbon tested is expressed in terms relative to methylcyclopentane, it is found that individual rates are independent of both hydrocarbon composition (Table II) and time (Table III).

TABLE II

NO INTERMOLECULAR EFFECT OF VARIATION IN HYDROCARBONS

	Relative specific activities		
Hydrocarbons present[a]	Isopentane	2,3-Dimethylbutane	2-Methylpentane
i-C_5, 2-MeC_5; 2,4-diMeC_5	0.37	...	0.17
i-C_5; 2,3-diMeC_4; 3-MeC_6	0.36	0.21	...
2,3-DiMeC_4; 2,3-diMeC_5; 2,2,4-triMeC_5	...	0.22	...
2-MeC_5; 2,2,4-triMeC_5; 2,2,5-triMeC_6	...	...	0.15

[a] Includes methylcyclopentane which was present to the extent of 25 vol. % in all cases; C_4 = butane, C_5 = pentane, C_6 = hexane.

TABLE III

EFFECT OF TIME

	Relative specific activities					
	Time, min.					
Hydrocarbon	10	20	30	60	120	180
Isopentane	0.40	...	0.44	0.29	0.32	0.35
2-Methylpentane	...	...	0.16	0.14	0.18	0.18
3-Methylpentane	0.15	0.14	0.15	...	...	...
2,4-Dimethylpentane	...	...	...	0.05	0.08	0.07
3-Methylhexane	0.06	0.05	0.06	...	...	...
2,2,4-Trimethylpentane	0.03	0.03	...	0.03	...	...
2,4- + 2,5-dimethylhexane	0.07	0.06	0.07	...	...	...

In several cases where thermodynamic equilibrium is fairly well established and the reaction involves production of only one other isomer, it is possible to compare measured compositions with thermodynamic values. These data are shown in Table IV. Product compositions have been measured starting with 2- and 3-methylpentane and 2,3- and 2,4-dimethylpentane. In each case, the other isomer was the only product observed. In all four cases, approach to equilibrium is about 75–90% complete. Since these compositions are based on tritium assay alone it could be argued that approaches to equilibrium are anomalously high because in each case the product formed has had more positions exposed for tritium incorporation. (For example: the cation from 2-methylpentane has eight exchangeable hydrogens. When it isomerizes to the cation of 3-methylpentane, two new hydrogens become available.) However, when a reaction has proceeded to the extent of 2–4 half-lives, a fair amount of product has returned to starting material and, in some cases, this could even further increase the number of exchangeable hydrogens. (Continuing the above example, it is possible that half the methyl groups in 2-methylpentane, re-formed from 3-methylpentane, will occupy the initial 4-position. This will lead to three additional exchangeable protons.) For this reason it is assumed that tritium assay is a reasonable representative of the actual chemical composition of those molecules that have undergone reaction.

TABLE IV

PRODUCT DISTRIBUTION APPROACHES THERMODYNAMIC EQUILIBRIUM[a]

Product compn.	Starting isomer		Thermodynamic equilibrium	
	2-MeC_5	3-MeC_5		32.2°[b]
2-MeC_5	75	60		67
3-MeC_5	25	40		33
	2,3-$DiMeC_5$	2,4-$DiMeC_5$	0°[c]	36.8°[d]
2,3-$DiMeC_5$	45	30	27	34
2,4-$DiMeC_5$	55	70	73	66

[a] C_5 = pentane. [b] A. Schriesheim and S. Koobiar, *J. Am. Chem. Soc.*, **82**, 832 (1960). [c] A. Schneider and E. J. Janoski, Preprints, Division of Petroleum Chemistry, 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962, Vol. 7, No. 1, p. 223. [d] G. M. Kramer and A. Schriesheim, *J. Phys. Chem.*, **65**, 1283 (1961).

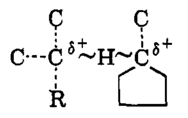
Figure 2 contains a plot of the data from Table I. In this case, relative rates are compared as a function of carbon number with the degree of substitution as a parameter. The only compound tested that did not contain a tertiary C–H bond, 2,2-dimethylbutane, underwent no exchange. This is consistent with previous information.[4,5,7] It would have been instructive to include isobutane in these comparisons, but the experimental procedure prohibited its use because of its volatility.

Discussion

Since exchange between carbonium ions and sulfuric acid is rapid compared to hydride transfer, it can be seen that the rate of tritium incorporation will be a measure of either the rate of ion formation (reaction 1) or regeneration (reaction 3). The data show that methylcyclopentane incorporates tritium 3 to 40 times faster than any of the hydrocarbons tested and it has generally been accepted that this naphthene is an excellent hydride donor.[8] This being the case, it is reasonable to assume that, for the paraffinic hydrocarbons, ion formation will be the rate-determining step.

It is apparent from Table I and Fig. 2 that the ease of ion formation drops off rapidly with increasing molecular weight. If a statistical correction is applied for those compounds containing two tertiary C–H bonds (the site of initial ion formation), it would appear that the rate of exchange depends solely on molecular weight (see Fig. 3). Inductive or hyperconjugative effects would, if anything, predict an increase in rate as the number of hydrogens contiguous to the tertiary center increased. Typical comparisons would be 2,3-dimethylbutane with 2,4-dimethylpentane and 2,2,3-trimethylbutane with 2,2,4-trimethylpentane. The expected increase is not observed. Two alternative explanations involve increased steric hindrance and decreased solubility in the acid phase as molecular weight increases.

Brown[9] has observed that 2,2,4-trimethyl-2-chloropentane solvolyzes some 22 times faster than *t*-butyl chloride and 13 times faster than *t*-amyl chloride. The explanation advanced involves a relief of B-strain as the halide leaves. In the present work 2,2,4-trimethylpentane ionizes more slowly than isopentane and presumably also more slowly than isobutane. The difference between solvolysis and hydride transfer lies in the fact that the former is unimolecular while the latter is bimolecular. In the transition state for hydride transfer the tertiary carbon–hydrogen bond must be partially bonded to both the starting material and the approaching carbonium ion, such as the methylcyclopentyl cation. The same factors which lead to B-



strain would also tend to inhibit hydride transfer because increased strain is developed in the transition state. That is, as the bulkiness of the R-group in the above example increases, it becomes more difficult for the approaching methylcyclopentyl cation to participate in the hydride-transfer reaction.

Decreased solubility may also have some bearing on the observed trends. Unfortunately, good data on the solubility of the hydrocarbons in question are not available and because of its reactivity the solubility of something like 2,2,4-trimethylpentane would be very difficult to measure. Even if such information were available one would have to know about the site of the reaction, whether at the interface or within the bulk acid phase. Hence, the contribution of relative solubilities is impossible to estimate.

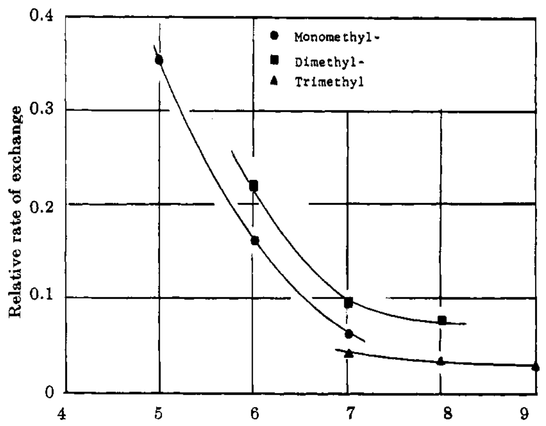


Fig. 2.—Effect of molecular weight on rate of exchange.

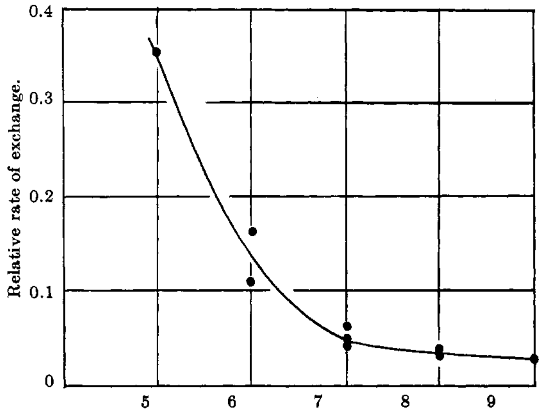


Fig. 3.—Effect of molecular weight on rate of exchange per tertiary C–H bond.

In those cases where isomerization is observed, the approach to equilibrium has an important bearing on reactions of a carbonium ion during its lifetime. The original data of Beeck and co-workers[4] suggested that not only does exchange occur with the acid but also that intramolecular hydride and methide shifts were rapid compared to intermolecular hydride transfer. The present work adds final evidence that methide and hydride shifts are in fact rapid compared to hydride transfer. In those cases where isomerization is possible, which does not involve a change in chain branching, there is a close approach to equilibrium. This must be the result of rapid intramolecular methide and hydride transfers.

In contrast, isomerizations involving a change in chain branching are not observed at low conversions. It has been postulated that such isomerizations take place *via* an alkylation and cracking sequence.[10] The products of this sequence would probably not show up until higher conversions were attained. Changes in chain branching are noted for some C_8 paraffins and this will be discussed at some length in the succeeding

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[7] K. N. Campbell and W. E. Erner, Office of Naval Research, Contract No. N7-ONR-439 (1950).

[8] H. Pines and J. M. Mavity, "Chemistry of Petroleum Hydrocarbons," Vol. 3, Reinhold Publishing Corp., New York, N. Y., 1955, p. 22.

[9] H. C. Brown and R. S. Fletcher, *J. Am. Chem. Soc.*, **71**, 1845 (1949).

[10] G. J. Karabatsos and F. M. Vane, *ibid.*, **85**, 729 (1963).

paper. However, based on the preceeding discussions, it is concluded that this observed "isomerization" is actually the result of side reactions rather than direct isomerization.

The preceeding data along with the work of others clearly demonstrate the primary reactions of simple aliphatic carbonium ions in sulfuric acid. Exchange with the acid and intramolecular methide and hydride shifts are rapid compared to intermolecular hydride transfer. When isomerization is possible, this occurs readily as long as a change in chain branching is not involved. With C_8 and higher hydrocarbons, β-fission of the carbonium ion can become a major reaction. Only those compounds containing tertiary C–H bonds will form carbonium ions and the ease of formation decreases with increasing molecular weight. This latter observation is attributed to steric shielding of the tertiary C–H bond or decreased solubility as the bulkiness of the alkyl groups increase.

Experimental

Tritiated sulfuric acid was prepared by mixing one volume of tritiated water (sp. act., 1 c./g.) with 500 volumes of 96.5% sulfuric acid. The resulting mixture had a specific activity of approximately 1 mc./g. Phillips pure grade hydrocarbons were used throughout except for 2,2,3-trimethylbutane which was obtained from the API.

A typical experiment was performed in the following manner. An equal volume mixture of three hydrocarbons and methylcyclopentane was prepared and 1 ml. was placed in a small (6-ml. capacity) glass vial. The tritiated sulfuric acid (1 ml.) was then added and the vial sealed with a polyethylene cap. The capped vial was clamped in a dental "Wig-L-Bug" shaker at room temperature and agitation begun. Samples were withdrawn and analyzed as a function of time by removing the vial, allowing the emulsion to settle, and withdrawing a small aliquot of the hydrocarbon with a Hamilton microliter syringe.

Analysis for chemical composition and radioactive content was performed on a radioassaying gas chromatograph that has been described previously.[2] Specific activities were calculated by dividing the area under the radio peak (output of the count rate meter) by the area under the chemical peak (output of the thermal conductivity cell), corrected for molar response.[11] The gas chromatograph used was a Perkin-Elmer Model 154 equipped with a 21-ft. column of Dow Corning silicone oil (DC-200) on Chromosorb. Operating conditions were 75° and 15-p.s.i.g. helium pressure.

In cases where a product was formed, composition was calculated by normalizing the area under the radio peaks. The total exchange rate of the starting compound was calculated by dividing the total areas of all radio peaks by the total areas of all chemical peaks. (In most cases, conversion was so low that products could not be measured on the normal chromatograph.)

Acknowledgment.—The author wishes to thank the Esso Research and Engineering Company for permission to publish this work, and, specifically, Drs. A. Schreisheim and S. Bank for their encouragement and suggestions.

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[11] A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, **31**, 230 (1959).

The Oxidation–Reduction Reaction of Hydrazinofluoro Aromatic Compounds. I. *para*-Substituted Perfluoro Aromatic Hydrazines

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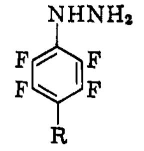
A novel reaction of hydrazinofluoro aromatic compounds has been observed. On reaction in strong base, the hydrazino function is subsequently lost as nitrogen and a substituent is displaced from either the *ortho* or *para* position. Evidence indicates that this is an internal oxidation–reduction reaction which proceeds through quinoid tautomerization. The relative leaving ability of the *para* substituents, for the series of *para*-substituted perfluorophenylhydrazines studied, was found to be $F > CF_3 >> C_6H_5 = H$.

In a previous paper[2] we described the reaction of hydrazine with pentafluorophenylhydrazine. The action of hydrazine as a nucleophile yielded the substitution product, 1,4-dihydrazinotetrafluorobenzene, whereas the competing reaction, yielding 1,2,4,5-tetrafluorobenzene and nitrogen, was attributed to the action of hydrazine as a base. In order to elucidate this reaction, *para*-substituted perfluoro aromatic hydrazines of the general class I were reacted with 3 *N* sodium hydroxide.



Ia, $R = F$
b, $R = NHNH_2$
c, $R = CF_3$
d, $R = H$
e, $R = C_6F_5$
f, $R = C_6H_5$

We propose that the reaction of pentafluorophenylhydrazine (Ia) in 3 *N* sodium hydroxide, and with hydrazine in dioxane, proceeds through the quinoid tautomers II and III. Subsequent 1,6- or 1,4-dehydrohalogenation leads to the intermediate diimide compounds IV and VI which, on spontaneous decomposition, afford the observed tetrafluorobenzenes V and VII (see Chart I).

Pentafluorophenylhydrazine (Ia) was prepared from chromatographically pure hexafluorobenzene[3] and was subjected to this reaction. The vapor phase chromatogram of the crude product showed it to be composed of 1,2,4,5-tetrafluorobenzene (V, 95.3%), 1,2,3,4-tetrafluorobenzene (VII, 1.7%), and pentafluorobenzene (3.0%). The pentafluorobenzene is believed to

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[1] This work was reported at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

[2] D. G. Holland, G. J. Moore, and C. Tamborski, *J. Org. Chem.*, **29**, 1562 (1964).

[3] We have observed that commercial grade hexafluorobenzene, from which pentafluorophenylhydrazine is prepared, contains several per cent of pentafluorobenzene.