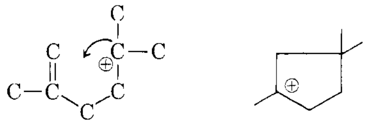
the latter role. Regardless of the interpretation, however, the inescapable conclusion is reached that "no alkylation occurs between isobutane and an olefin in sulfuric acid until this isobutane 'activator' has built up."

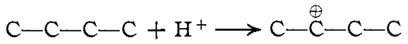
The question of how these materials are produced is of some importance and evidence is available on how they are formed. Traces of trimethylcyclopentanes were produced during the alkylation of 2,5-dimethyl hexadiene-1,5 with isobutane and these naphthenes undoubtedly arose from the intramolecular alkylation of the unsaturated cation I.



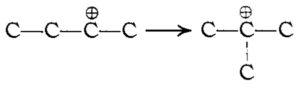
I II (16)

Hydride exchange between isobutane and molecule II would lead to 1,1,3-trimethylcyclopentane while dehydrogenation by hydrogen transfer would lead to the cyclic diene. Similar mechanisms have been postulated for the production of high molecular weight unsaturates in Friedel–Crafts reactions.[14]

Expansion of this mechanism to include the other butylenes is obvious. For example, it is well known that in sulfuric acid the alkylate products from butene-1 and butene-2 are nearly identical.[15] This is explained on the basis of a rapid isomerization equilibration between the two. At normal reaction temperatures, 0–20°, equilibrium favors butene-2 by a factor of about 10 to 1. Hence, it can be assumed that regardless of whether the reactant is butene-1 or -2, it is the alkylation of butene-2 that is under consideration. The initial step in the alkylation of butene-2 is protonation (step 17) followed by rearrangement to the more stable tertiary carbonium ion (step 18). Data obtained at this Laboratory, to be published shortly,[11,13] clearly demonstrate these two steps.



$$\mathrm{C{-}C{-}C{-}C} + \mathrm{H}^{+} \longrightarrow \mathrm{C{-}\overset{\oplus}{C}{-}C{-}C} \qquad (17)$$



$$\mathrm{C{-}C{-}\overset{\oplus}{C}{-}C} \longrightarrow \mathrm{C{-}}\underset{\underset{\mathrm{C}}{|}}{\overset{\oplus}{\mathrm{C}}}\mathrm{{-}C} \qquad (18)$$

The exact extent of this isomerization is unknown. The present argument requires that it only occurs to a sufficient extent to initiate the reaction. The reaction path after step 18 is identical to the mechanism outlined for isobutylene.

Acknowledgment.—The authors would like to acknowledge the Esso Research and Engineering Co. for their permission to publish this work.

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[14] A. Schriesheim and S. Khoobiar, "Proceedings of the International Catalyst Society," Paris, 1960.

[15] S. F. Birch, *et al.*, *Ind. Eng. Chem.*, **31**, 884 (1939); **31**, 1079 (1939).

[CONTRIBUTION FROM THE ESSO RESEARCH AND ENGINEERING CO., LINDEN, N. J.]

Ionic Reactions Occurring During Sulfuric Acid Catalyzed Alkylation. II. Alkylation of Isobutane with C^{14}-Labeled Butenes

BY J. E. HOFMANN AND A. SCHRIESHEIM

RECEIVED AUGUST 18, 1961

The sulfuric acid catalyzed alkylation of isobutane with C^{14}-labeled butylenes was studied in continuous flow equipment. Product analyses and C^{14}-distribution determinations were obtained for the initial products and for the products formed at steady-state conditions. It was found that initial product stemmed primarily from olefin polymerization reactions, while at steady-state the predominant reaction was direct alkylation. In addition, a considerable difference in reactivity between butene-1 and isobutylene was observed with isobutylene having a greater tendency to polymerize. Radioactive carbon distributions show that the formation of fragments smaller than octanes proceed *via* the scission of a $C_{12}^{\oplus}$ intermediate. It is concluded that the transition from initial product to steady-state occurs as a result of a buildup of an isobutane solutizer or active hydride transfer agent.

Introduction

The acid catalyzed isoparaffin–olefin alkylation reaction has been the subject of considerable study since first described by Ipatieff[1] and has been the subject of comprehensive reviews by Kennedy[2] and Schmerling.[3] However, formulation of a detailed mechanism for the reaction has been based upon indirect evidence. For instance, in the low temperature acid-catalyzed reaction between isobutane and butylenes, no direct evidence is available on the mechanism of formation of fragments such as pentanes, hexanes and heptanes.

In addition to this lack of knowledge, certain pecularities have arisen in the reaction mechanism[4,5] when comparing fresh with equilibrium or "steady-state" sulfuric acid catalyst. In this case, "steady-state" acid is defined as that which has been in use for a length of time sufficient to produce a product of constant composition. In order to study the whole reaction in more detail, a study was made of the alkylation of isobutane with radio-labeled butenes. The C^{14}-content of all the products could be followed and these data would lead to more direct information regarding the detailed mechanism of the alkylation reaction. Previous studies[4] also dictated that because the acid does change with

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[1] V. N. Ipatieff, "Catalytic Reactions of High Pressures and Temperatures," The Macmillan Co., New York, N. Y., 1936, pp. 673–701.

[2] R. M. Kennedy, "Catalysis," Vol. 6, Reinhold Publ. Corp., New York, N. Y., 1958, pp. 1–41.

[3] L. Schmerling, "The Chemistry of Petroleum Hydrocarbons," Vol. 3, Reinhold Publ. Corp., New York, N. Y., 1955, pp. 363–408.

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

[5] T. D. Stewart and W. H. Calkins, *ibid.*, **70**, 1006 (1948).

time, the experiments must be carried out on a continuous basis, since the product composition is a function of catalyst life.

As a result of this study, it will be shown that the reaction mechanism is not as simple as heretofore believed and that the mechanism undergoes marked changes as the acid catalyst life increases. Evidence will be presented showing that the formation of products other than octanes proceed primarily through a C$_{12}$-intermediate. Finally, the results may be interpreted on the basis of a buildup in the acid phase of an isobutane activator (solutizer) or efficient hydride transfer agent.

Experimental

All experimental work was performed in the same equipment described in the previous paper of this series.[4] The only modification was the addition of a separate reactant charge cylinder to contain the blend of isobutane and radiolabeled butylene. Provision was included for alternation between the two-reactant charge cylinders each containing reactants of essentially identical concentrations. The radiolabeled reactants were used only during the initial and equilibrium stages of the reaction. The interim transition period was made up with non-radioactive reactants. Nominal experimental conditions were: 10°, 50 p.s.i.g., 15/1 mole ratio of isobutane to butylene and olefin space velocities of 0.05 and 0.30 vol. of olefin/hr./vol. of acid in the reaction zone. The fresh acid was 97.7 wt. % H$_2$SO$_4$ from the American Cyanamid Co.

Periodically, the total product is analyzed for both composition and radioactive content by injecting a sample into a radioassaying gas chromatograph. The radioassaying unit consists of a Perkin-Elmer model 154B gas chromatograph followed directly by an internal flow proportional Geiger counter.[6] This apparatus enables a simultaneous analysis for both composition and radioactive content of each peak as it is eluted from the chromatograph.

Hydrocarbon reagents used during this study were Matheson research grade isobutane and C.P. grade olefins. The C^{14}-labeled olefins were obtained from the Research Specialties Co. and had a specific activity of 0.01 millicurie/millimole. The position of labeling was in the 2-position for isobutylene and the 1-position of butene-1.

The results regarding the C^{14}-content of product fractions are reported on the basis of relative specific activity (R.S.A.). The R.S.A. is the measured specific activity of each product divided by the specific activity of the reactant olefin. Thus, if a product molecule incorporated one molecule of olefin, the relative specific activity of the product would be 1.0.

Results

Table I shows both the chemical compositions and the relative specific activity (RSA) for each of the product components in fresh and steady-state acid using C^{14}-labeled butene-1. In accordance with previous studies[4] selectivity to the octane fraction improved markedly as the life of the acid increased. The most striking result is the difference in specificity of the various product fractions for fresh and steady-state catalyst. Thus, the RSA of the pentane through heptane fractions drops considerably on going to the steady-state catalyst period.

TABLE I

Acid	Fresh[a]		"Steady-state[b]	
	Comp., mole %	R.S.A.	Comp., mole %	R.S.A.
i-C$_5$	10.6	0.88	4.9	0.31
23 DMC$_4$, 2 + 3 MC$_5$	12.0	1.07	4.1	.37
23 + 24 DMC$_5$, 223 TMC$_4$	8.4	1.27	3.6	.49
224 TMC$_5$	23.0	1.03	36.5	.80
24 + 25 DMC$_6$	8.9	1.45	10.6	.78
233 + 234 TMC$_5$, 23 DMC$_6$	26.3	1.32	38.7	.90
224 + 225 TMC$_6$	10.8	2.11	1.6	1.06

[a] Based on first 3 hours of operation. [b] Based on operation after 21 hours.

When the olefin feed rate is increased from 0.05 to 0.30 vol./hr./vol., thereby decreasing residence time to 1/6 its initial value, there is another slight change in both composition and RSA. These data are shown in Table II. The RSA of the C$_5$ through C$_7$ fractions increases as the space velocity increases from 0.05 to 0.30 vol./hr./vol.

TABLE II

Olefin space velocity, v./hr./v.	0.05		0.30	
	Comp., mole %	R.S.A.	Comp., mole %	R.S.A.
i-C$_5$	4.9	0.31	6.9	0.36
23 DMC$_4$, 2 + 3 MC$_5$	4.1	.40	6.6	.43
23 + 24 DMC$_5$, 223 TMC$_4$	3.6	.56	5.5	.56
224 TMC$_5$	36.5	.73	26.4	.80
24 + 25 DMC$_6$	10.6	.68	9.2	.69
233 + 234 TMC$_5$, 23 DMC$_6$	38.7	.77	42.3	.84
224 + 225 TMC$_6$	1.6	1.16	3.3	.96

Table III summarizes the data for fresh and "steady-state" catalyst with isobutylene as the reactant. In general, the selectivity to the total octanes and to trimethylpentanes in particular is not as high for isobutylene as it is for butene-1. Again, the most striking data involve the C^{14}-content of the various fractions. The trimethylpentane fractions show very little C^{14} while the dimethylhexanes and other fractions have a relatively high C^{14}-content.

TABLE III

Acid	Fresh[a]		"Steady-state"[b]	
	Comp., mole %	R.S.A.	Comp., mole %	R.S.A.
i-C$_5$	17.9	0.80	11.2	0.58
23 DMC$_4$, 2 + 3 MC$_5$	9.2	1.05	6.5	.67
23 + 24 DMC$_5$, 223 TMC$_4$	8.1	1.70	6.8	.92
224 TMC$_5$	28.5	0.50	33.3	.26
24 + 25 DMC$_6$	9.8	1.55	10.7	.75
233 + 234 TMC$_5$, 23 DMC$_6$	24.6	0.59	29.0	.28
224 + 225 TMC$_6$	1.9	1.46	2.6	.78

[a] Based on the first 4 hours of operation. [b] Based on operation after 50 hours.

In addition to C^{14} appearing in the pentane and heavier product fractions, some C^{14} was also found in the isobutane fraction. The percentage of total activity appearing in the isobutane fraction was 23% for butene-1 at "steady-state" and 38% for isobutylene at "steady-state." In order to compare the results on a consistent basis, it was assumed that one molecule of non-radioactive butylene was formed for each C^{14}-containing butylene that was saturated to form isobutane. The RSA's of the product fractions were proportionally increased to account for the loss of activity to isobutane. These data are summarized in Table IV. (A detailed justification for this is included in the Discussion section.)

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(6) R. Wolfgang and F. S. Rowland, *Anal. Chem.*, **30**, 903 (1958).

TABLE IV

	Rel. sp. act.				
	$C_4^{=}$-1			i-$C_4^{=}$	
	Fresh[a]	S.S.[a]	S.S.[b]	Fresh[a]	S.S.[a]
i-C_5	0.95	0.4	0.45	1.07	0.94
23 DMC_4, 2 + 3 MC_5	1.15	.48	.52	1.40	1.08
23 + 24 DMC_5, 223 TMC_4	1.37	.64	.69	2.30	1.55
224 TMC_5	1.03	1.04	.96	0.67	0.42
24 + 25 DMC_6	1.50	1.01	.83	2.07	1.21
233 + 234 TMC_5, 23 DMC_6	1.28	1.17	1.01	0.79	0.45
224 + 225 TMC_6	2.12	1.38	1.28	1.95	1.26

[a] At 0.05 v./hr./v. olefin space velocity. [b] At 0.30 v./hr./v. olefin space velocity.

Discussion of Results

Conversion of a portion of the reactant olefin to isobutane is consistent with considerable data on the self-alkylation of olefins.[7-9] The reaction involves transfer of hydrogen from isobutane to the reactant olefin and then alkylation of the resulting isobutylene with isobutane. The over-all reaction can be expressed according to eq. 1 and 2. The quantitative amount of self-alkylation observed

$$C_nH_{2n} + i\text{-}C_4H_{10} \longrightarrow C_nH_{n+2} + i\text{-}C_4H_8 \qquad (1)$$

$$i\text{-}C_4H_8 + i\text{-}C_4H_{10} \longrightarrow i\text{-}C_8H_{18} \qquad (2)$$

with butene-1 and isobutylene is in agreement with data obtained by Hofmann.[10] It is on this basis that the relative specific activities of the product fractions have been corrected for the amount of self-alkylation. In other words, the effective specific activity of the reactant olefin is reduced to varying degrees depending on the amount of self-alkylation. The correction is made to place all results on a consistent basis of a constant specific activity for the reactant olefin. Henceforth, the discussions will be concerned only with the data presented in Table IV.

Previous work[4] at this Laboratory has shown that rather low alkylate yields, *ca.* 50 mole %, were obtained with fresh sulfuric acid. The hypothesis was advanced that these low yields were due to a lack of availability of isobutane leading to considerable olefin polymerization. This hypothesis is substantiated by considering the data in columns 1 and 2 of Table IV. The pentane, hexane and heptane fractions produced in fresh acid contain a considerably larger portion of olefin than the same fractions obtained with "steady-state" acid and this must be due to olefin polymerization followed by acid cracking. In addition, these results provide insight into the mechanism of formation of the pentane, hexane and heptane fractions. The ratio of the R.S.A.'s of the C_5 to C_6 to C_7 fractions for all the experiments with butene-1 is essentially constant, 1.0/1.21/1.44 for column 1, 1.0/1.20/1.60 for column 2 and 1.0/1.16/1.53 for column 3.

The only reasonable interpretation of these data is to postulate the buildup of a C_{12}-intermediate followed by scission of this species (or its isomers) to pentanes, hexanes and heptanes. A similar scheme has been previously postulated by Schneider and Kennedy during their study of the alkyl fluoride initiated reactions of isoparaffins and olefins in HF–BF_3 media.[11,12]

If a C_{12}-fragment containing a uniform distribution of C^{14} were to split into C-$_5$, C_6- and C_7-fragments, the ratio of activities would be 1.0/1.2/1.4. The agreement between theory and experimental values for butene-1 indicates that the C_5- through C_7-fractions come from scission of a C_{12}-intermediate and that methide shift in the C_{12} and its precursors is rapid compared to C_{12} cracking. The latter results follow from the data showing that a uniform C_{14}-distribution is reached among the pentane, heptane and hexane fractions.

Assuming this to be the case, then it is possible to back calculate the R.S.A. of the C_{12}-intermediate and to elucidate the mechanism of formation of this intermediate. In fresh acid the C_{12} would have an R.S.A. of 2.3, or on the average, the C_{12} would contain 2.3 molecules of olefin and 0.7 molecule of isobutane. With "steady-state" catalyst the R.S.A. of the C_{12} is only about 1.0. At "steady-state," the C_{12} contains only one molecule of olefin and two molecules of isobutane. Thus, in fresh acid C_{12} comes primarily from olefin polymerization (sequence I) while at equilibrium, C_{12} arises from an alkylation sequence. The initial alkylation step is followed by proton loss and subsequent alkylation of the octene (sequence II).

Sequence I

$$i\text{-}C_4^{14} = \; + H^{\oplus} \longrightarrow t\text{-}C_4^{14\oplus} \qquad (3)$$

$$t\text{-}C_4^{14\oplus} + i\text{-}C_4^{14=} \longrightarrow C_8^{2\,(14)\oplus} \qquad (4)$$

$$C_8^{2(14)\oplus} + i\text{-}C_4^{14=} \longrightarrow C_{12}^{3(14)\oplus} \qquad (5)$$

Sequence II

$$t\text{-}C_4^{\oplus} + i\text{-}C_4^{14=} \longrightarrow C_8^{14\oplus} \qquad (6)$$

$$C_8^{14\oplus} \longrightarrow C_8^{14=} + H^{\oplus} \qquad (7)$$

$$t\text{-}C_4^{\oplus} + C_8^{14=} \longrightarrow C_{12}^{14\oplus} \qquad (8)$$

Clearly, product from fresh acid is deficient in isobutane and hence this provides direct evidence that there is a buildup within the acid phase of an "activator" that makes isobutane available for reaction. Whether this is the effect of increased solubility or the buildup of a hydride transfer intermediate cannot be deduced from these data.

Increasing the rate of olefin addition from 0.05 to 0.3 v./hr./v. shows a slight increase in the R.S.A.'s of the C_5-, C_6- and C_7-fractions. As olefin feed rate is increased the steady-state olefin concentration undoubtedly is increased and one would expect that reaction between octyl carbonium ions and olefins would start to become important (reaction 9). The occurrence of this reaction would lead to a slight increase in the C^{14} content of the $C_{12}^{\oplus}$ intermediate.

$$i\text{-}C_8^{14} + C_4^{14} = \; \longrightarrow C_{12}^{2(14)\oplus} \qquad (9)$$

Therefore, the fragments from cracking at the higher olefin addition rate would also show a slight increase in their radioactive content.

Formation of nonanes during alkylation is most probably the result of secondary reactions. Direct scission of a $C_{12}^{\oplus}$ to C_9- and C_3-fragments is not considered important since no propane is formed

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(7) S. H. McAllister, *et al.*, *J. Org. Chem.*, **6**, 647 (1941).

(8) L. Schmerling, *J. Am. Chem. Soc.*, **67**, 1778 (1945).

(9) L. Schmerling, *ibid.*, **68**, 275 (1946).

(10) J. E. Hofmann, unpublished data.

(11) A. Schneider and R. M. Kennedy, *J. Am. Chem. Soc.*, **73**, 5013, 5017, 5024 (1951).

(12) A. Schneider, *ibid.*, **76**, 4438 (1954).

during the reaction and the activity of the C_7-fraction indicates that it was not formed by alkylation of propylene with isobutane. If the C_9 resulted from alkylation of isopentane, formed during reaction 11, with butylene, the expected R.S.A. of the nonane fraction would be 1.0 for the olefin plus the R.S.A. of the pentane fraction. The data presented in columns 1 and 2 of Table IV come very close to supporting this hypothesis.

Insufficient material with a molecular weight higher than nonane was present, so that it was impossible to obtain analyses on these fractions. However, it is known that decanes, undecanes and dodecanes are formed during the reaction[2,3] and sufficient information is available from the previous discussions to predict the route of formation of this fractions. Decanes and undecanes would come from alkylation of butylene with isohexanes and isoheptanes, respectively (reactions 13, 14). The C_6- and C_7-fragments themselves are formed by reactions 10 and 11. Dodecanes undoubtedly arise from saturation of the $C_{12}^{\oplus}$ intermediate by hydride transfer with isobutane (reaction 15).

$$C_{12}^{\oplus} \nearrow t\text{-}C_6^{\oplus} + i\text{-}C_6^{=} \qquad (10)$$

$$C_{12}^{\oplus} \searrow t\text{-}C_5^{\oplus} + i\text{-}C_7 \text{ or } C_5^{=} + t\text{-}C_7^{\oplus} \qquad (11)$$

$$t\text{-}C_5^{\oplus} + i\text{-}C_4^{=} \longrightarrow t\text{-}C_9^{\oplus} \xrightarrow{RH} i\text{-}C_9 \qquad (12)$$

$$t\text{-}C_6^{\oplus} + i\text{-}C_4^{=} \longrightarrow t\text{-}C_{10}^{\oplus} \xrightarrow{RH} i\text{-}C_{10} \qquad (13)$$

$$t\text{-}C_7^{\oplus} + i\text{-}C_4 \longrightarrow t\text{-}C_{11}^{\oplus} \xrightarrow{RH} i\text{-}C_{11} \qquad (14)$$

$$t\text{-}C_{12}^{\oplus} \xrightarrow{RH} i\text{-}C_{12} \qquad (15)$$

The data obtained with isobutylene as the reactant olefin, columns 4 and 5 of Table IV, were quite surprising and more difficult to interpret. There is a general drop in the activity of the various fractions going from fresh to "steady-state" catalyst, but the decrease is not as pronounced with isobutylene as it is with butene-1. The most striking data are the segregation of C^{14}, with relatively little C^{14} appearing in the trimethylpentanes. Obviously, the majority of the trimethylpentanes do not arise as a result of the alkylation of isobutane with isobutylene-C^{14}. The most plausible explanation for these data involves rapid polymerization of the reactant isobutylene followed by cracking and hydrogen transfer reactions which produce non-radioactive isobutylene, *in situ*. This non-radioactive isobutylene is highly dispersed and alkylated selectively to trimethylpentanes. A mechanistic scheme for this is presented in reactions 16 through 19.

$$3\ i\text{-}C_4^{14=} \longrightarrow i\text{-}C_{12}^{14\oplus} \qquad (16)$$

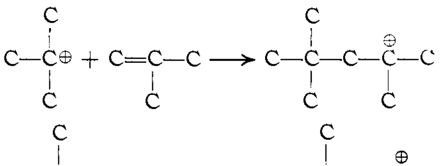
$$i\text{-}C_{12}^{14\oplus} \longrightarrow C_7^{14=} + i\text{-}C_5^{14\oplus} \qquad (17)$$

$$i\text{-}C_4 + C_7^{14=} \longrightarrow C_7^{14} + i\text{-}C_4^{=} \qquad (18)$$

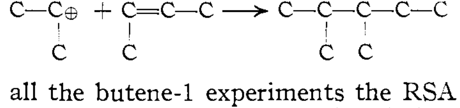
$$i\text{-}C_4 + i\text{-}C_4^{=} \longrightarrow i\text{-}C_8 \qquad (19)$$

The difference between isobutylene and butene-1 apparently arises from the known fact that butene-1 does not polymerize very rapidly. Also, the isobutylene that is produced by hydrogen transfer during butene-1 alkylation, step 18, is not completely separated from the general body of reactant olefin. The proposed mechanism for isobutylene requires almost complete segregation of the tagged $iC_4^{=}$ of step 16 from the untagged $iC_4^{=}$ of step 19. This will be the case if the polymerization of tagged isobutylene occurs rapidly at the acid interface followed by the slow release of untagged isobutylene into the acid phase.

Close inspection of the data from butene-1 suggests that segregation of feed olefin and isobutylene formed *in situ* may be occurring here too, although to a lesser extent. Classically, the initial fragments produced from isobutylene and butene-2[13] would be the 224 and 223 trimethylpentyl cations, respectively (reactions 20 and 21).



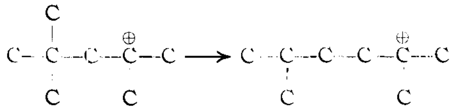
$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{}^{\oplus} + C{=}\underset{C}{C}{-}C \longrightarrow C{-}\underset{C}{\overset{C}{C}}{-}C{-}\underset{C}{\overset{\oplus}{C}}{-}C} \qquad (20)$$



$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{}_{\oplus} + \underset{C}{C}{=}C{-}C \longrightarrow C{-}\underset{C}{\overset{C}{C}}{-}\underset{C}{C}{-}\overset{\oplus}{C}{-}C} \qquad (21)$$

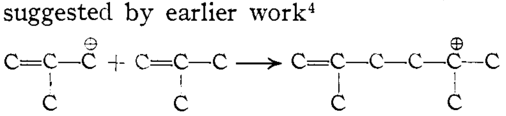
In all the butene-1 experiments the RSA of the 224 trimethylpentane fraction is slightly lower than that of the other trimethylpentanes. This may be an indication that the 224 isomer is the partial result of alkylation involving the nonradioactive isobutylene formed *in situ*. However, the selectivity is small and certainly does not approach the degree of segregation observed when isobutylene is the reactant olefin.

Another point of interest arising from the isobutylene data concerns the relative amount of activity in the trimethylpentane and dimethylhexane fractions. With both fresh and equilibrium catalyst the ratio of the RSA's for dimethylhexanes to trimethylpentanes is about 3 to 1. Clearly, formation of dimethylhexanes is not solely due to rearrangement of a trimethylpentyl cation (reaction 22) since if this were the case, the expected RSA ratio would be 1.0.



$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{-}C{-}\underset{C}{\overset{\oplus}{C}}{-}C \longrightarrow C{-}\underset{C}{C}{-}C{-}C{-}\underset{C}{\overset{\oplus}{C}}{-}C} \qquad (22)$$

Other paths such as cracking of the $C_{12}^{\oplus}$ and dimerization of isobutylene *via* an allylic ion (reaction 23) must also contribute to dimethylhexane formation. Dimerization *via* an allylic ion was suggested by earlier work[4]



$$\mathrm{C{=}\underset{C}{C}{-}\overset{\ominus}{C} + C{=}\underset{C}{C}{-}C \longrightarrow C{=}\underset{C}{C}{-}C{-}C{-}\underset{C}{\overset{\oplus}{C}}{-}C} \qquad (23)$$

and it was demonstrated that 2,5-dimethyl-1,5-hexadiene could be saturated to 2,5-dimethylhexane in the presence of sulfuric acid and isobutane. It is impossible to say which path is most important and dimethylhexane formation may in fact proceed *via* several routes at once.

In conclusion, it is apparent that these data support the hypothesis that an isobutane "activator"

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[13] Although the reactant olefin used during this study was butene-1, it has been generally accepted that there is a rapid equilibrium between the 1- and 2-isomers prior to alkylation. Since thermodynamics favor the 2-isomer by a factor of about 10 to 1 at 10°, butene-2 will make up the major portion of the reaction olefin.

must be formed in the acid phase before alkylate product is obtained selectively and in close to theoretical yield. Secondly, it has been shown that formation of products other than the octanes proceeds primarily *via* a C_{12}-cation intermediate. At low olefin concentration (low space velocity) the $C_{12}^{\oplus}$ comes from alkylation of isobutane with octene. At higher olefin concentration the reaction between octyl cations and butylenes begins to become important. Finally, it has been found that the reactivity of normal and isobutylene under alkylation conditions is considerably different and this leads to vast differences in the formation of alkylate products.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY, NEW YORK 53, N. Y.]

Structure and Reactivity in Carbonyl Reactions; Temperature Coefficients of Rate of Formation of Several Thiosemicarbazones[1]

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Rates of thiosemicarbazone formation of seven carbonyl compounds of a variety of structural types have been measured at 25 and 50° in aqueous solution buffered at *p*H 7, using a spectrophotometric method of analysis. Thiosemicarbazone formation for all the compounds investigated is a second-order reaction, and reversible, except for furfural, under the experimental conditions of the investigation. Determination of temperature coefficients of rate permitted the calculation of relative thermodynamic activation quantities. A previously suggested correlation between presumed rigidities of carbonyl compounds and their corresponding activation quantities was not observed. This finding agrees in part with a previous report respecting oxime formation but disagrees with the results established for semicarbazone formation. However, an excellent linear free energy relationship was obtained when the logarithms of the specific rates for thiosemicarbazone formation were plotted against the logarithms of specific rates for semicarbazone formation. The linearity of the free energy relationship suggests the essential validity of the two series of data, the fundamental similarity of the three reaction systems, and the advisability of further study of this particular phase of structure and reactivity. Attempts to obtain linear correlations with Taft σ^*-values failed. In addition, some original spectral data are reported for seven thiosemicarbazones.

Introduction

An especially trenchant analysis of the general problem of structure and reactivity has been presented by Hammett.[2] In addition, Price and Hammett[3] have discussed the effect of structure on reactivity for carbonyl reaction systems and indicated that an explanation of the effect of structural change on reaction rate based exclusively on potential energy effects is valid only where there is a cancellation of other effects due to kinetic energy steric effects. An investigation of temperature coefficients of reaction rate is prerequisite to the determination of the importance of kinetic energy steric effects. Price and Hammett[3] measured the temperature coefficients of the rate of semicarbazone formation and found a parallelism between molecular rigidity and entropy of activation, which is indicated by the data of columns one and two in Table VI. In addition, they proposed that the parallelism would apply with high probability to other typical carbonyl reactions. The parallelism was found subsequent general confirmation in the reaction of benzaldehyde with both acetone and methyl ethyl ketone[4]; in the acid-catalyzed hydration of isobutene, trimethylethylene and 1-methylcyclopentene-1 by aqueous acid[5]; in the hydrolysis of esters catalyzed by ion-exchange resins[6]; in the reaction of methyl iodide with certain amines in nitrobenzene[7,8] and in thiosemicarbazone formation of several alkylbutyrophenones.[9]

In 1956, Fitzpatrick and Gettler,[10] in an attempt to obtain additional support for the Hammett parallelism and to extend the range of its validity, measured the temperature coefficients of rate of oximation. Derived relative entropies of activation are listed in Table VI, column 3, and an examination reveals little or no parallelism between rigidity of structure and entropy of activation.

To resolve this apparent divergence, temperature coefficients of reaction rate of thiosemicarbazone formation were measured, since thiosemicarbazone formation resembles semicarbazone formation more closely, formally or otherwise, than does oximation.

Experimental

Materials.—Thiosemicarbazide hydrochloride (Matheson, Coleman and Bell Inc.) was further purified, stored, and its purity was determined by the method of Price and Hammett.[3] The purified material possessed an acidimetric titer which was within two parts per 1,000 of its iodometric titer.

All carbonyl compounds were distilled in all-glass apparatus before use. Eastman Kodak Co. compounds: acetone was redistilled, b.p. 56.0°; diethyl ketone was redistilled, b.p. 101.5°; methyl ethyl ketone was redistilled, b.p. 79–80°; cyclohexanone was redistilled, b.p. 154–155°; furfural was first redistilled at atmospheric pressure, then further purified by vacuum distillation, b.p. 60–61° at

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(1) Abstract of a dissertation submitted by Irwin S. Fiarman in partial fulfillment of the requirements for the degree of Master of Science in the Faculty of the Graduate School of Arts and Sciences, New York University.

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