This constancy, independent of the electron-attracting properties of the group which is *para* to the alkyl, is just what one would expect if only the contributions to the moment discussed above were operative. The result does not appear consistent with the idea that hyperconjugation makes an important contribution. If hyperconjugation were operative in these systems its importance would increase in, for example, the benzonitriles as compared with the alkylbenzenes because of the contribution from the resonance structure

$$H_3{}^+=C=\!\!\!\left\langle\underline{\quad}\right\rangle\!\!\!=C=N^-$$
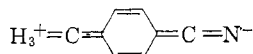
If it is granted that C–H hyperconjugation is more important than C–C, then the spread in corrected moments should decrease in the benzonitriles and nitrobenzenes (and to a lesser extent in the phenylacetylenes), as compared with the alkylbenzenes. This is not observed to be the case, except in the nitrobenzenes where a small decrease is noted.

The increase in corrected moment upon substitution of methyl for the ring hydrogen in each series can be ascribed to the polarization of the C_{alkyl}–C_{ring} bond and adjacent C–H bonds, as discussed above. The subsequent small increase on substitution of methyl for hydrogen in the alkyl group is assigned to the greater induced moments in the C–C bonds as compared with the C–H.

Finally, the encouraging fact should be noted that the corrected moments for the bromobenzenes are relatively the same as for the other series, although the correction in these compounds is of opposite sign.

These results do not by any means rule out the possibility that hyperconjugative interactions between the alkyl group and the ring exist, but they do place some limit on their importance in affecting the electron distribution in the molecule. In addition they serve to emphasize the importance of considering the polarizabilities of alkyl groups in discussing their effect on molecular properties.

B. The Effect of Solvent.—Schubert and co-workers have advanced the hypothesis that steric inhibition of solvation is important in determining the apparent order of electron release by alkyl groups in systems where an electron-demand is measured.[7,17] In order to test the effect of solvent on the dipole moments, the *p*-alkylbenzonitriles were studied in dioxane and chloroform solutions. From the data in Table II it is clear that the spread in moments is significantly smaller in dioxane than in cyclohexane. Dioxane, although essentially non-polar, is nevertheless basic in character and is presumably capable of solvating electron-deficient sites in the solute molecules. If the corrections for induced moments are applied to these results a Baker–Nathan order will result.

The dipole moments calculated from the measurements on chloroform solutions have no particular significance as regards their absolute magnitude; it is well recognized that correct values of dipole moment cannot be determined by measurements in polar solvents.[18] Nevertheless for a series of molecules of similar dipole moment and molecular shape the effect of the polar solvent should be the same on all of the compounds in the series, so that the relative values may have significance. Whether this is true or not, it can simply be noted that the spread in apparent moments is again smaller than in the cyclohexane solutions.

URBANA, ILLINOIS

Stereospecific Isomerization of Butene-1 to Butene-2 over SiO₂–Al₂O₃ Catalyst

BY P. J. LUCCHESI, D. L. BAEDER AND J. P. LONGWELL

The double bond isomerization of butene-1 to *cis*- and *trans*-butene-2 has been studied over silica–alumina catalyst. With either neutron irradiated or ordinary catalyst, the isomerization was observed to be stereospecific. The thermodynamically unfavored *cis*-butene-2 is kinetically favored and the *cis/trans* ratio is decidedly in favor of the *cis*-form, especially at low conversions. This result cannot be reconciled with conventional carbonium ion theory.

Introduction

Recent work in this Laboratory has been concerned with the effect of neutron pre-irradiation on the activity of silica–alumina catalysts for the isomerization of butene-1 to *cis*- and *trans*-butene-2. The results of this work, which are reported in a separate paper, showed that neutron pre-irradiation decreased the catalytic activity of silica–alumina. Only the catalytic activity of the catalyst was affected by radiation, since it was found that at a given degree of conversion the product distribution was the same for irradiated and ordinary catalysts, the product consisting almost entirely of *cis*- and *trans*-butene-2. Of greater interest than the observed effect of neutron irradiation was the finding that the isomerization is markedly stereospecific, since the thermodynamically unfavored *cis*-isomer is kinetically favored, especially at low conversions. The stereospecific nature of this reaction is discussed in the present paper.

Experimental

Catalysts and Reagents.—The catalyst used in this work was Davison SiO₂–Al₂O₃ (13 wt. % alumina) pressed into

pills approximately $^3/_{16}''$ in diameter and $^3/_{16}''$ high. The butene-1 was 99.9+ purity material. The catalyst was pretreated by heating for 16 hr. at 1000°F., then for 3 hr. at 1250°F. The catalyst then was cooled and portions of it were sealed in separate aluminum containers. The catalyst in one container (650 cc.) was exposed for 16 days in the water of a swimming atomic reactor and integrated flux levels of 6.1×10^{18} thermal neutrons/cm., 6.9×10^{18} fast neutrons/cm., and 1.2×10^{10} R./hr. γ-radiation. During exposure, the catalyst was at an average temperature of 220°F. Portions of total catalyst that were not irradiated were in all other respects treated in exactly the same way as the irradiated catalysts.

Catalytic Tests.—The catalysts were tested by studying the isomerization of butene-1 to butene-2. These experiments were made at 150°F. and atmospheric pressure in a conventional non-recycle flow unit. The flow reactor was charged with 200 cc. (127 g.) of catalyst, and the conversion of butene-1 to butene-2 was followed by infrared analysis of the gaseous product. The products were mainly *cis*- and *trans*-butene-2, with only a trace of isobutene. The analytical determination and the composition data reported in this paper are considered reliable to ±1%.

Results and Discussion

Table I gives typical conversion data for butene-1 as a function of time at different rates of flow. The data are presented for both irradiated and non-irradiated SiO_2-Al_2O_3 catalyst. However, the only effect of neutron exposure was to decrease the activity of the catalyst. The selectivity remained unchanged, as shown in Fig. 1, since at a given degree of
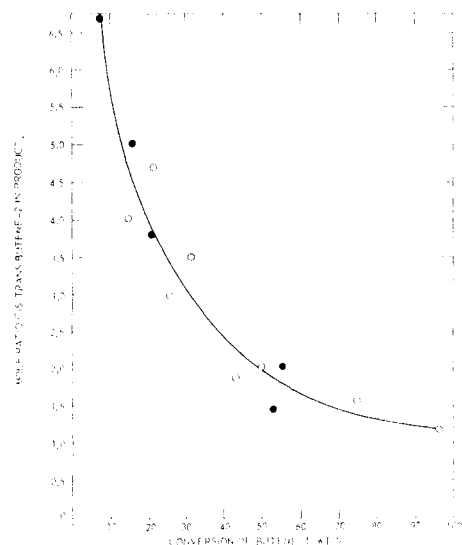
Fig. 1.—Ratio of *cis*- to *trans*-butene-2 as a function of butene-1 conversion over irradiated SiO_2-Al_2O_3 catalyst (●) and unirradiated catalyst (O) at atmospheric pressure and 150°F.

conversion of butene-1 the products were the same for both catalysts. Therefore for the purposes of this paper, the catalysts are identical and are so considered in the following discussion.

As evident from Fig. 1, the isomerization of butene-1 to butene-2 over SiO_2-Al_2O_3 catalyst at 150°F. goes predominantly to *cis*-butene-2 at low conversions. Since the ratio of *cis/trans* butene-2 in the product increases sharply at lower degrees of butene-1 isomerization, the *cis*-isomer is formed preferentially, although this isomer is the less stable one predicted from thermodynamics. In other words, the isomerization is markedly stereo-
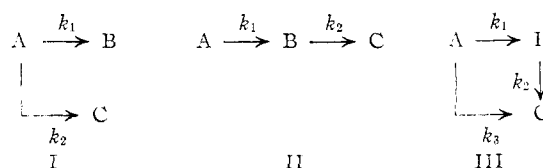
TABLE I

NON-IRRADIATED CATALYST

Butene-1 feed rate, g./hr.	Time, hr. since start of run	Cumulative, g. feed fed to catalysts	Butene-1 conv., wt. %
120	2.25	270	42.9
60	4.25	390	50.4
12	9.25	450	96.5
120	9.80	516	26.0
120	10.55	606	21.5
60	12.55	726	31.8
12	17.55	786	75.2
120	18.35	882	15.1

IRRADIATED CATALYST

Butene-1 feed rate, g./hr.	Time, hr. since start of run	Cumulative, g. feed fed to catalysts	Butene-1 conv., wt. %
120	1.38	165	10.0
60	3.38	285	20.7
12	8.38	345	55.5
120	9.18	441	8.4
60	11.18	561	16.3
12	16.18	621	53.5
120	16.93	711	6.8

specific. It recently has been reported[1] that acid-catalyzed dehydration of butyl alcohol can be stereospecific in that the less stable *cis*-butene-2 is sometimes produced in higher concentrations than predicted thermodynamically. However, the authors are not aware that such a stereospecific process has been reported for the double bond migration in olefins.

Examination of the *cis/trans* butene ratio at various concentrations of butene-1 gives further insight into the mechanism of the double bond migration. If A, B and C represent butene-1, *cis*-butene-2 and *trans*-butene-2, respectively, there are three reasonable reaction paths to consider. These paths are designated I, II and III

$$\begin{array}{ccc} A \xrightarrow{k_1} B & A \xrightarrow{k_1} B \xrightarrow{k_2} C & A \xrightarrow{k_1} B \\ | & & \quad\; k_2 \downarrow \\ \llcorner\!\!\rightarrow C & & \llcorner\!\!\rightarrow C \\ k_2 & & k_3 \\ I & II & III \end{array}$$

Scheme I is excluded because it would predict a constant *cis/trans* ratio regardless of butene-1 conversion and this is not observed experimentally. However, if scheme II is considered, it is easily shown that assuming $k_1 = k_2$, the concentration of *cis*-butene-2 is related to that of butene-1 by equation 1

$$X_2 = -X_1 \ln X_1 \qquad (1)$$

where X_2 is the mole fraction of *cis*-butene-2 and X_1 the mole fraction of butene-1 present at a given time. The experimentally observed concentrations are compared in Fig. 2, with the values predicted from equation 1. For reasons explained above, data obtained with both pre-irradiated and non-irradiated catalyst are included. As evident from Fig. 2, the experimental data from both irradiated and unirradiated catalyst fit equation 1 very well up to butene-1 conversions of 55%.

(1) H. Pines and W. D. Haag, presented at 133rd Meeting of Am. Chem. Soc., San Francisco, Calif., April, 1958.

Scheme III will not predict the observed composition data. Furthermore, the data at low butene-1 conversion clearly show that the direct conversion of butene-1 to the *trans*-butene-2 isomer is much slower than the conversion to *cis*-butene-2. Therefore, k_3 is small and scheme II is the most plausible kinetic scheme with $k_1 = k_2$. This means that butene-1 is isomerized to *cis*-butene-2 with about the same rate constant as the latter isomerizes to *trans*-butene-2. However, *cis*-butene-2 is formed preferentially.

The acid-catalyzed double bond migration in olefins is commonly considered a carbonium ion reaction[2] proceeding by proton attachment to the olefin to form the ion followed by proton elimination from another part of the carbonium ion and formation of a new double bond. However, classical carbonium ion theory predicts that proton addition to either butene-1 or *cis*-butene-2 gives the same intermediate carbonium ion, secondary butyl ion. Therefore, classical carbonium ion theory cannot account for the stereospecific nature of double bond migration, since the intermediate complex is identical and there is no reason why the conversion of butene-1 to *trans*-butene-2 should first go through the *cis*-isomer.

The situation is different if the proton addition to butene-1 is considered from the so-called non-classical point of view. In such additions, the proton has been visualized as pi-complexing at the double bond. The reaction of butene-1 would then be visualized as resulting from a concerted series of reactions in which the pi-complex is formed and the three position carbon atom donates a proton back to the surface. From this point of view, the intermediate ions in the isomerization of butene-1 and *cis*-butene-2 are represented by structures IV and V, respectively

IV   V

These two ions are very similar in the sense that their formation should involve about the same activation energy. Therefore, if this step is considered rate controlling, the approximate equality

(2) A. G. Oblad, T. H. Milliken and G. A. Mills, "Advances in Catalysis," Vol. III, Academic Press, Inc., New York, N. Y., 1951.

between k_1 and k_2 is understandable. The stereospecificity of the reaction can now be pictured as a result of structure IV, which prevents the free rotation of the number one carbon to a position
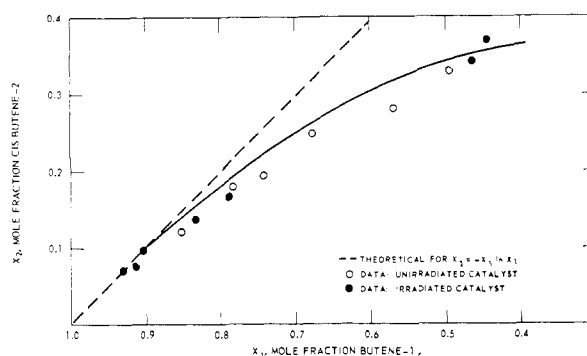

Fig. 2.—Comparison of experimental product composition with predicted composition assuming butene-1 $\xrightarrow{k_1}$ *cis*-butene-2 $\xrightarrow{k_2}$ *trans*-butene-2 and $k_1 = k_2$. Data obtained at atmospheric pressure and 150°F.

trans relative to carbon atom number four. This leads to the *cis*-butene-2 as the desorbed product. The *cis*-isomer can then adsorb and add a proton to give structure V, and this structure now easily passes over to the end product—*trans*-butene-2.

While this approach is admittedly speculative, it does account for the stereospecificity experimentally observed. Further, it would predict that the rate constants k_1 and k_2 should be approximately equal since both reactions involve, as the rate-controlling step, the protonation of a double bond. Undoubtedly, there are other possible explanations. In fact, the possibility that the apparent equality between k_1 and k_2 is fortuitous cannot be excluded. The experimental fact is perhaps of greater importance than the postulated mechanism, because the observed stereospecificity of the double bond migration of butene-1 provides new insight into acid-catalyzed organic reactions.

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