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Carbon Black-Catalyzed Olefin Isomerization

II. Kinetics of a Three-Membered, First-Order, Reversible System

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The carbon black-catalyzed interconversion of 2-ethyl-1-butene (A1), *cis*-3-methyl-2-pentene (A2), and *trans*-3-methyl-2-pentene (A3) has been studied using a computerized kinetic analysis. The computer analysis has been augmented by more traditional but less rigorous kinetic treatment. The isomerizations in slurry are observed to occur at moderate temperatures by first-order, reversible processes. The values of all six empirical rate constants in the reaction system have been determined. The selectivity of formation of A2 and A3 from A1 is temperature independent. The activation energy for disappearance of A1 is 16.1 ± 2 kcal/mole. These results have been interpreted in terms of a mechanism consisting of protonation of adsorbed olefin to form a single, common tertiary carbonium ion.

INTRODUCTION

Catalyzed isomerization of olefins is usually not amenable to rigorous kinetic analysis because too many chemical species are involved and the reactions are reversible. Wei and Prater, who refer to such complex reactions as "highly coupled systems," have developed a method for obtaining relative values for all rate constants using linear algebra (*1*). The Wei and Prater method has not been applied very widely. Several applications are given in the original paper including the catalyzed interconversion of *n*-butenes. The *n*-butene system has also been analyzed by an extension of this method developed by Lombardo and Hall (*2*). The only other reports of applications that were found are zeolite-catalyzed isomerization of xylenes (*3*) and *n*-pentene (*4*). One of the purposes of this paper is to provide another application of the Lombardo and Hall extension of the Wei and Prater method for analysis of complex reaction systems.

A second purpose is to elucidate the surface chemistry of carbon black particles by determining their catalytic properties in olefin isomerization. Carbon black properties are of interest in uses such as rubber reinforcement, pigmentation, and adsorption and as a catalyst support. Double bond shifts (*5*) and methyl migrations (*6*) have been reported to take place following protonation of adsorbed olefin by Brönsted acid groups on the surface of channel black particles. Since the occurrence of surface groups having sufficient protonating power to protonate double bonds would not have been predicted, additional support for the proposed mechanism was thought to be desirable. In the work reported here the kinetic analysis of isomerization of another set of isomers was undertaken to test the proposed ionic mechanism and to indicate the generality of the mechanism. The reaction system studied consists of inter-

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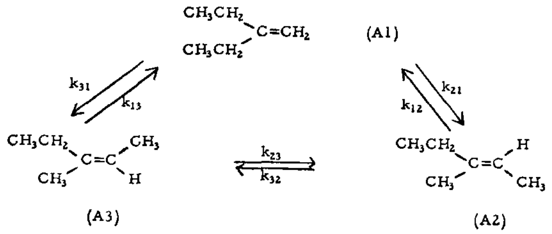
conversion of three isomers: 2-ethyl-1-butene (A1), *cis*-3-methyl-2-pentene (A2), and *trans*-3-methyl-2-pentene (A3).



(1)

According to the definitions proposed by Wei and Prater this is a "monomolecular system." In his review, Boudart (*7*) uses the term "reaction network" to refer to these complex systems and, in place of "monomolecular system," uses the phrase "network of first-order, reversible reactions."

Kagawa (*8*) has recently discussed the relationship between empirical rate constants obtained by the Wei and Prater analysis and the rate constants for elementary steps in a Langmuir–Hinshelwood mechanism.

METHODS

The computer method of Lombardo and Hall was used in this study, but programs were rewritten for compatibility with an IBM 360 Model 50 computer. Furthermore, a different subroutine (*9*) was used to calculate composition at any desired time for any specified initial composition using the rate constants obtained from the main program as input. The computation of compositions from known rate constants had been described previously for complex systems (*10*). The program used in this study is available (*11*).

The procedure for carrying out kinetic runs included degassing 0.250-g samples of carbon black catalysts at 100°C in a vacuum system capable of maintaining a pressure of 10^{-6} Torr (1 Torr = 133.3 N m^{-2}) as measured by a McLeod gauge. About 15 ml of olefin, previously dried over sodium or Drierite, was vacuum distilled onto the degassed catalyst, and dry nitrogen was admitted until the system was at atmospheric pressure. Reactions were run with a slight positive pressure of nitrogen. Water has been shown to have a strong inhibitory effect (*5*). The slurry was stirred magnetically; however, the stirrer was turned off several minutes before samples were withdrawn to allow the carbon black to settle. A syringe was used to remove 0.1- to 0.2-ml samples for analysis by gas chromatography. Runs were carried out at 18, 30, 40, 50, and 60°C. Procedural details are presented elsewhere (*11*).

Olefins were obtained from Phillips Petroleum Co., pure grade, and from Chemical Samples Co. The carbon black samples were obtained from Cabot Corporation. Two high oxygen channel blacks were used as catalysts. A channel black of lower oxygen content was found to be inactive without intentional oxidation of the surface. The black used most extensively is identified by the supplier as Black Pearls 2 (BP-2). This black consists of particles having an average diameter of about 1.2×10^{-6} cm, a surface area of about 744 m^2/g, and a bound oxygen content of 9.5% (*12*). Only several runs were made with the second channel black, Peerless II (P-II). It has a particle diameter of about 2.2×10^{-6} cm and a surface area of 300 m^2/g (*11*). The surface acidity as indicated by hydrogen–deuterium exchange

TABLE 1

Relative Rate Constants at 60°C for Runs Beginning with Pure 2-Ethyl-1-butene over Channel Blacks

Catalyst (run)	k_{23}/k_{13}	k_{21}/k_{13}	k_{31}/k_{13}	k_{21}/k_{13}	k_{32}/k_{13}
BP-2 (1)	6.46	19.0	25.8	1.44	12.7
BP-2 (2)	2.57	18.8	26.7	1.47	5.97
BP-2 (3)	5.20	18.3	29.1	1.37	11.3
BP-2 (4)	4.64	18.8	28.6	1.35	9.57
P-II (1)	2.06	15.3	23.4	1.35	4.25

from adsorbed D_2O is 1.3 mequiv/g for BP-2 and 1.1 mequiv/g for P-II (*13*).

RESULTS

Relative rate constants obtained by the Lombardo and Hall extension of the Wei and Prater method are given in Table 1. The first four entries are for runs with BP-2 as catalyst; the last entry is for a run with P-II as catalyst. Care was taken to use uniform procedures throughout in an attempt to reproduce surface conditions as closely as possible from run to run. Despite these precautions, significant variations were observed from run to run especially for the rate constants for interconversion of A2 and A3. Variations in the relative rate constants for interconversion of A1 and A2 and of A1 and A3 are not as great. Run 2 in particular is at variance with other BP-2 results. This run was observed to proceed much more slowly than the other runs with BP-2. Time is not part of the input for the kinetic analysis by the extended Wei and Prater method; however, the conditions that caused a slow reaction in run 2 may also have contributed to the low values of k_{23} and k_{32} obtained in this run. Since water has been shown to be an effective poison (*5*), the variations observed in the first four entries are thought to result from our inability to control water contamination at low levels of contamination.

The variations from run to run with one carbon black are of about the same magnitude as the change noted when that black is replaced by a slightly less oxidized channel black, as indicated by the last entry in Table 1. Better control of surface contamination would be required before any conclusions concerning the effect of the nature of particular channel blacks could be drawn. However, a black having a considerably lower acidic hydrogen content (Spheron 6, 0.3 mequiv/g) had no catalytic activity as received, but it did catalyze the isomerizations following oxidation in an oxygen stream at elevated temperatures. The absolute rate of isomerization over P-II was substantially lower than the average for BP-2; at 60°C the half-life was 39.4 min for P-II, and the average half-life for BP-2 was 18.8 min. Thus, it appears that absolute constants are more sensitive than relative constants to the catalyst used.

The average values of the relative constants given in Table 1 were used to compute the composition along various reaction paths originating at selected initial compositions. The paths predicted from this computation are shown as solid lines in Fig. 1. Experiments were run with olefin mixtures corresponding to selected initial compositions, and the experimentally determined compositions are indicated as data

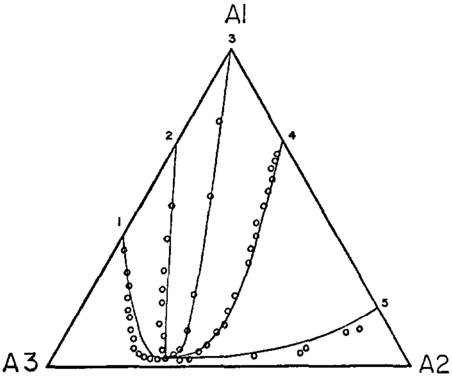


FIG. 1. Reaction paths for interconversion of 2-ethyl-1-butene and *cis*- and *trans*-3-methyl-2-pentene at 60°C with BP-2 as catalyst. The solid lines are all predicted paths based on rate constants obtained from path 3. Circles represent experimental data points.

points in Fig. 1. Path 3 corresponds to the one from which the rate constants were determined, and as expected the fit is best for this path. Only the points from experiment BP-2 (1) (Table 1) are indicated along path 3.

Determinations of relative rate constants were carried out at a series of temperatures with the results indicated in Table 2. Once again the results for interconversion of A2 and A3 are apparently subject to error because there is considerable variation without a clear-cut trend. The selectivity for isomerization of A1 over BP-2 can be obtained at each temperature by dividing the entry in the fifth column by that in the fourth column of Table 2. In Table 3 selectivities calculated in this way are compared with those obtained by the more traditional procedure of extrapolating product ratios to zero time. The results in Table 3 indicate that for 2-ethyl-1-butene the variation in selectivity with temperature is negligible and that this conclusion would be reached regardless of the method of determination. The absence of variation in the selectivity for formation of A2 and A3 with temperature indicates that $E_{21} - E_{31} = 0$ where E's represent empirical activation energies. Division of entries in the sixth column by corresponding entries in the seventh column of Table 2 yields k_{12}/k_{32} as a function of temperature so that $(E_{12} - E_{32})$ should be available. Unfortunately the scatter is such that no firm conclusions can be drawn concerning this difference in activation energies. The third column should yield $E_{23} - E_{13}$, but once again the problems in reproducibility, apparently associated with water contamination, prevent a firm conclusion.

TABLE 2

Average Values of Relative Constants Obtained with BP-2 Catalyst at Several Temperatures

Temperature (°C)	Number of runs	k_{23}/k_{13}	k_{21}/k_{13}	k_{31}/k_{13}	k_{12}/k_{13}	k_{32}/k_{13}
60	4	4.72	18.7	27.6	1.41	9.89
50	2	4.26	19.4	28.6	1.40	8.78
40	4	5.87	20.6	30.6	1.38	12.1
30	3	4.13	21.8	33.0	1.36	8.5
18	2	7.31	24.2	35.4	1.37	14.5

TABLE 3

Temperature Independence of Selectivity of Formation of *cis*- and *trans*-3-Methyl-2-pentene from 2-Ethyl-1-butene.

Temperature (°C)	k_{21}/k_{31}	$([A2]/[A3])_{t=0}$
60	0.676[a]	0.688[b] (3)
50	0.678	0.670 (1)
40	0.673	0.663 (4)
30	0.661	0.638 (3)
18	0.684	0.710 (2)

[a] By Wei and Prater-type analysis.

[b] By extrapolation of product ratios. Each number in parentheses indicates the number of results that were averaged to yield the number reported.

Where pure A1 is used as reactant, the concentrations of A2 and A3 can be considered negligible at low conversions. Therefore, the rate expression for disappearance of A1 can be approximated by a first-order

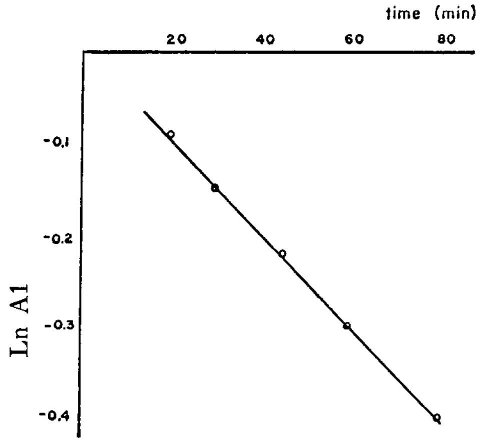


Fig. 2. First-order plot for disappearance of 2-ethyl-1-butene up to 33% conversion at 40°C with BP-2 as catalyst. The slope = $k_{21} + k_{31}$ = 0.00518 min^{-1}.

TABLE 4

Absolute Values of First-Order, Reversible Rate Constants at 40°C with BP-2 Catalyst

k_{21}	k_{31}	k_{12}	k_{32}	k_{13}	k_{23}
1.99[a]	3.19	0.129	0.494	0.102	0.243

[a] 10^{-3} min^{-1} in all cases.

rate expression,

$$-d[\mathrm{A1}]/dt = (k_{21} + k_{31})[\mathrm{A1}]. \quad (2)$$

A first-order plot is given up to 33% conversion in Fig. 2. From the slope of this plot and the k_{21}/k_{31} ratio obtained for the same run by the method described previously, it is possible to calculate the absolute values of k_{21} and k_{31} at 40°C. Combination with other rate constant ratios permits evaluation of the absolute values of all rate constants at 40°C, as indicated in Table 4. A similar treatment at other temperatures allows evaluation of k_{21} (and other constants) as a function of temperature. Thus, it is possible to prepare an Arrhenius plot as indicated in Fig. 3. The activation energy is 16.1 ± 2 kcal/mole; the large uncertainly reflects the effect of unequal levels of water contamination. Within each run the first-order fit is excellent, but the rate constants are not easily reproduced from run to run, apparently because the catalyst drying procedure does not produce identical levels of water contamination.

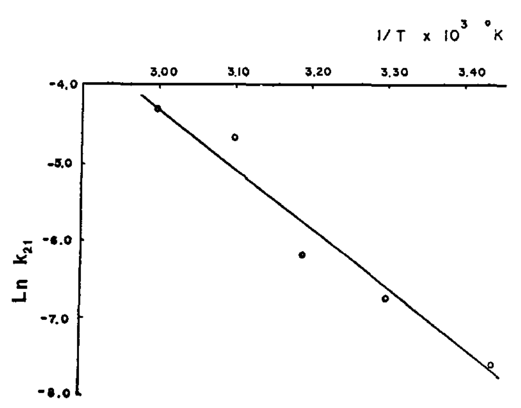
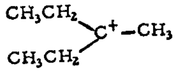


FIG. 3. Arrhenius plot for k_{21} in the range 18 to 60°C using BP-2 as catalyst. The slope corresponds to an activation energy of 16.1 ± 2 kcal/mole.

DISCUSSION

The fit, in Fig. 1, of experimental reaction paths (data points) to those predicted (solid lines) from the relative rate constants reported in Table 1 is sufficient to confirm that the reaction system under consideration is a first-order reversible network. The discrepancies between experimental and predicted values are probably the result of variations in rate constants caused by residual water contamination. It should be emphasized that in construction of Fig. 1, the average rate constants were obtained from just four runs, all starting with pure A1. Undoubtedly a better overall fit could have been achieved if all paths had been used to obtain average values of rate constants. This procedure, however, would have reduced the impact of the illustration of the predictive power obtained from a single curved reaction path using the Lombardo and Hall extension of the Wei and Prater method.

The fact that nonzero values were obtained for all relative rate constants indicates that all paths in reaction (1) exist. This result eliminates all mechanisms in which equilibration occurs sequentially (such as A1 ⇄ A2 ⇄ A3) rather than concurrently as depicted in reaction (1). The mechanism proposed previously for 2-methyl-1-pentene and 2-methyl-2-pentene equilibration under comparable conditions involves protonation to form a tertiary carbonium ion intermediate (*5*). A simple ionic mechanism with a common adsorbed intermediate, I, is also consistent with the kinetic data reported here. Product identification indicates that


$$(CH_3CH_2)_2C^{+}-CH_3$$

I

protonation to form secondary or primary carbonium ions does not occur at a significant rate.

The absence of variation in product selectivity with temperature for conversion of A1 to A2 and A3 suggests that the activated complex lying between A1 and the intermediate, I, has the highest potential energy of the three activated complexes lying between network members and I.

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