

TABLE I

	1-CF ₃			4-CF ₃			3-F		
	ϕ^{*a}	$J(1,3)^b$	$J(1,4)^b$	ϕ^{*a}	$J(4,1)^b$	$J(4,3)^b$	ϕ^{*a}	$J(3,1)^b$	$J(3,4)^b$
<i>trans</i>	+64.804 ±0.002	24.72 ±0.05	1.27 ±0.02	+68.350 ±0.002	1.33 ±0.01	5.49 ±0.04	+113.669 ±0.005	24.76 ±0.05	5.38 ±0.02
<i>cis</i>	+62.180 ^c ±0.002	8.67 ±0.08	11.32 ±0.07	+66.274 ^c ±0.001	11.43 ±0.08	7.74 ±0.04	+106.761 ±0.008	8.09 ^d ±0.06	8.09 ^d ±0.06

^a Concentration 20% by volume in CCl₃F. ^b The theoretical first order multiplicities were observed in every case. ^c Assigned by analogy to the *trans* case, since the virtual identity of coupling constants for the two CF₃ groups precluded positive identification. ^d The peak is a 7-fold binomial multiplet, resulting from nearly equal coupling to the two CF₃ groups. An explanation for the "J-averaging" phenomenon has been given by J. I. Musher, *J. Chem. Phys.*, **36**, 1086 (1962).

separations of the peaks as compared to the coupling constants, a simple first-order spin-spin analysis was entirely sufficient. Shielding values, ϕ^{*10} and coupling constants for the two isomers are presented in Table I.

The *trans* isomer was identified readily by virtue of the narrow ($J = 1.3$ c./sec.) quadruplet CF₃ peaks.⁶ The large doublet splitting of one of these peaks, $J = 24.74$ c./sec., is not observed for the *cis* isomer and thus must not be $J(3,4)$, since both isomers contain exactly the same structure at these positions and would be expected to show coupling constants of similar magnitude. It therefore must be $J(1,3)$, and thereby identifies the peak due to fluorines at the 1-position. Since this large coupling constant is observed only when fluorine is located *cis* to a CF₃ group, it serves to verify the previously unsupported assignments.^{1,4} The J -values for the *cis* isomer are in satisfactory agreement with the literature values.^{1,4,6} Owing to the accidental near-equivalence of $J(1,3)$ and $J(3,4)$ the assignment of CF₃ peaks must be based on the substantial difference in ϕ^{*} -values between the CF₃ peaks for each isomer. The 3.8 ± 0.3 p.p.m. decrease in shielding, attributed to the presence of Cl rather than F on the olefinic carbon atom bearing the CF₃ group, also is observed in other related compounds.⁶

ADDED IN PROOF.—A recent paper by Andreades¹² also has verified the original assignments.

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(10) G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 781 (1959).

(11) G. V. D. Tiers, *ibid.*, **62**, 1151 (1958).

(12) S. Andreades, *J. Am. Chem. Soc.*, **84**, 864 (1962).

INTERACTION OF HYDROCARBONS WITH Pt-Al₂O₃ IN THE PRESENCE OF HYDROGEN AND HELIUM

By J. C. ROHRER and J. H. SINFELT

Esso Research and Engineering Co., Linden, N. J.

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In studies of the chemisorption of hydrocarbons on various metals, Kemball and co-workers^{1,2} have shown that extensive decomposition takes place, leading to the formation of hydrogen deficient surface residues. The excessive dehydrogenation leading to the formation of such residues also may be accompanied by polymerization reactions. This type of irreversible chemisorption would be expected to limit severely the catalytic activity of the surface for various hydrocarbon reactions. This has been strikingly illustrated in the present work for two different reactions over a platinum on alumina catalyst, the dehydrogenation of

(1) P. G. Wright, P. G. Ashmore, and C. Kemball, *Trans. Faraday Soc.*, **54**, 1892 (1958).

methylcyclohexane to toluene and the dehydrocyclization of *n*-heptane to toluene.

Experimental

A micro-reactor technique, similar to that described by other investigators,^{3,4} was used to follow catalytic activity. Small shots of liquid reactant, about 0.05 ml., were injected into either helium or hydrogen in the inlet line leading to the reactor. The pressure was maintained at 1.7 atmospheres. Carrier gas rates of 500 and 1500 cc. (STP) per minute were used for the helium and hydrogen, respectively. A catalyst charge of 1.0 gram was used throughout. The reaction products were analyzed by gas chromatography. Details of the reactor and chromatographic analyses have been presented elsewhere.⁵ The hydrocarbons used were Phillips pure grade (>99 mole % pure) in all cases. Both the hydrocarbons and hydrogen were dried to less than 5 p.p.m. water by procedures described previously.⁵ The catalyst employed in this work contained 0.3 wt. % platinum on alumina, and was prepared by impregnation of alumina with aqueous chloroplatinic acid. The surface area of the alumina was approximately 145 m.²/g.

Results

Successive shots of methylcyclohexane were injected into hydrogen and helium carrier gases, and the activity of the catalyst for dehydrogenation to toluene at 315° was determined.

Shot no.	Carrier gas ^a	Mole % toluene formed
1	H ₂	21
2	H ₂	19
3	H ₂	20
4	He	22
5	He	6.5
6, 7, 8 ^b	He	
9	He	1.7
10 ^c	H ₂	14
11	H ₂	15

^a H₂ rate = 1500 cc. (STP) per min.; He rate = 500 cc. (STP) per min. ^b No product analyses obtained. ^c 48-hour H₂ treatment between periods 9 and 10.

During the period when hydrogen carrier gas was used, the conversion to toluene remained constant at about 20 mole %. Equilibrium conversion at these conditions corresponds to about 85 mole % toluene.⁶ When the carrier gas was switched to helium, the first shot gave about the same conversion as was observed in hydrogen. How-

(2) A. K. Galwey and C. Kemball, *ibid.*, **55**, 1959 (1959).

(3) R. J. Kokes, H. Tobin, Jr., and P. H. Emmett, *J. Am. Chem. Soc.*, **77**, 5860 (1955).

(4) A. I. M. Keulemans and H. H. Voge, *J. Phys. Chem.*, **63**, 476 (1959).

(5) J. H. Sinfelt and J. C. Rohrer, *ibid.*, **65**, 978 (1961).

(6) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," API Research Project 44, Carnegie Press Inc., New York, N. Y., 1953.

ever, since the helium flow rate was threefold lower than that of hydrogen, and the residence time in the case of helium therefore threefold greater, the initial catalytic activity in the presence of helium is substantially lower. Furthermore, the conversion in the presence of helium was found to decline markedly with each successive shot, declining from 22 to 1.7 mole % after six shots. After passing hydrogen over the catalyst for 48 hr., however, about 75% of the catalytic activity was regained, as evidenced by the 15 mole % conversion obtained in the presence of hydrogen.

Some similar data also were obtained with *n*-heptane. In this case, the activity of the catalyst for dehydrocyclization of the *n*-heptane to toluene at 471° was determined for successive shots of *n*-heptane.

Shot no.	Carrier gas ^a	Mole % toluene formed
1	H ₂	15
2	He	11
3	He	0.6
4	He	0.4
5, 6, 7, 8, 9 ^b	He	
10	He	0.1
11	H ₂	6.6

^a H₂ rate = 1500 cc. (STP) per min.; He rate = 500 cc. (STP) per min. ^b No product analyses obtained.

Again, in the presence of helium, the initial catalytic activity was substantially lower than in the presence of hydrogen, and the conversion to toluene declined markedly with successive shots. Also, when the carrier gas was switched back to hydrogen, much of the catalyst activity was regained.

The deactivation observed with successive shots appears quite definitely to be due to the hydrocarbon being passed over the catalyst in the absence of hydrogen, rather than to the presence of helium itself. This is supported by the observation that prolonged treats with pure helium (5 hr.) prior to the first hydrocarbon shot in helium did not affect the initial conversion to toluene.

These studies illustrate in a striking manner the rapid decline in catalytic activity which occurs when a hydrocarbon is contacted with platinum catalyst in the absence of hydrogen. As indicated by the work of Kemball and co-workers,^{1,2} the chemisorption of hydrocarbons on metals is accompanied by extensive decomposition to form hydrogen-deficient surface residues. The role of hydrogen then appears to be one of removal of residues, thus maintaining the surface active for catalytic reactions. Evidence for the removal of surface residues from a platinum catalyst has been obtained by Pitkethly and Goble.⁷ These investigators studied the adsorption of benzene on supported platinum catalysts, and found that the adsorption was almost totally irreversible at temperatures above 200°. However, adsorption sites were recovered by treatment with hydrogen, which removed the adsorbed surface residues by hydrocracking reactions leading to the formation

(7) R. C. Pitkethly and A. G. Goble, Paper No. 91, Section II, Proceedings of the Second International Congress on Catalysis, Paris, France (1960).

of C₁-C₄ hydrocarbons. It was concluded also that hydrogen can maintain a steady-state concentration of hydrocarbon-free platinum sites, which presumably would be active for catalytic reactions.

IONIC ASSOCIATION AND CORRELATION BETWEEN DOUBLE LAYER STRUCTURE AND ELECTRODE KINETICS

By PAUL DELAHAY AND AKIKO ARAMATA

Coates Chemical Laboratory, Louisiana State University, Baton Rouge 3, Louisiana

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The possibility of ion pair formation *solely in the double layer region* at the electrode in charge transfer reactions was suggested in a previous paper¹ from this Laboratory. It was discussed in some detail by Frumkin^{2,3} to account for certain features of current-potential curves for the reduction of anions. Ion pair formation outside the double layer was not considered. Formation of ion pairs in the bulk of the solution was discussed recently by Joshi and Parsons,⁴ together with other interpretations, to account for the properties of the electrical double layer at the interface between mercury and mixtures of barium chloride and hydrochloric acid. The influence of ion pair formation in the bulk of solution in the correlation between double layer structure and electrode kinetics was also considered **qualitatively** by Gierst⁵ and Parsons⁶ in the interpretation of the minimum which appears in current-potential curves for the reduction of K₂S₂O₈ under certain conditions. A quantitative interpretation of the ion-pair effect is given here for the reduction of iodate on mercury in alkaline solutions of varying composition. This electrode reaction is advantageous because it occurs in a range of potentials in which there is very little specific adsorption of the ions involved. Application is made of the corrected Tafel plot recently mentioned in a previous paper from this Laboratory.⁷

Experimental

Experimental methods were quite conventional and have been reported previously.⁷ Adsorbable impurities (organic) were removed by treatment with activated charcoal as noted before. The solution of KOH was titrated. The K₄Fe(CN)₆ solution was prepared from the dehydrated salt and was titrated for verification.⁸

A five-compartment cell was used with the following electrodes: hydrogen electrode in I; dropping mercury electrode or capillary of Lippmann electrometer and platinum cylinder for differential capacity measurements in III; a high-resistance saturated calomel electrode inserted in IV; and a mercury pool in V. Junctions between compart-

(1) P. Delahay and C. C. Mattax, *J. Am. Chem. Soc.*, **76**, 5314 (1954).

(2) A. N. Frumkin, *Trans. Faraday Soc.*, **55**, 156 (1959).

(3) A. N. Frumkin, "Transactions of the Symposium on Electrode Processes," E. Yeager, ed., John Wiley and Sons, New York, N. Y., 1961, p. 1.

(4) K. M. Joshi and R. Parsons, *Electrochim. Acta*, **4**, 129 (1961).

(5) L. Gierst, ref. 3, pp. 109-144.

(6) R. Parsons, "Advances in Electrochemical Engineering," Vol. 1, P. Delahay, ed., Interscience Division, John Wiley and Sons, New York, N. Y., 1961, pp. 1-64.

(7) K. Asada, P. Delahay, and A. K. Sundaram, *J. Am. Chem. Soc.*, **83**, 3396 (1961).

(8) I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1957, p. 135.