

3. DJERASSI, C., AND GUTZWILLER, J., *J. Am. Chem. Soc.* **88**, 4537 (1966).
4. BIELLMANN, J. F., AND LIESENFELT, H., *Compt. Rend.* **263C**, 251 (1966); *Bull. Soc. Chim. Fr.*, p. 4029 (1966).
5. YOUNG, J. F., OSBORN, J. A., JARDINE, F. H., AND WILKINSON, G., *Chem. Commun.*, p. 131 (1965).
6. CRAMER, R., *J. Am. Chem. Soc.* **88**, 2272 (1966).

A. L. ODELL
J. B. RICHARDSON
W. R. ROPER

*Urey Radio Chemical Laboratory
The University of Auckland
Auckland
New Zealand*

Received June 1, 1967

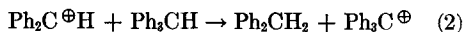
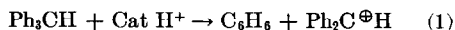
Mechanism of Triphenylcarbonium Ion Formation on the Silica-Alumina Surface

Leftin and Hall (1) noted that the triphenylcarbonium ion formed spontaneously from triphenylmethane on silica-alumina, but they were unable to ascertain unambiguously the fate of the H^- which is stoichiometrically removed in the process. However, they showed that it was not evolved as H_2 by reaction with catalyst protons, nor was it transferred to a carbonium ion formed from an olefinic impurity. Since treatment of the catalyst with H_2 at 500° had no effect on the reaction, they argued that oxidation of triphenylmethane to triphenylcarbinol was not a necessary prerequisite for carbonium ion formation. On the basis of this information, they suggested that the hydride ion was abstracted and held by the silica-alumina surface, presumably by strong Lewis acid sites which had been frequently postulated.

Recently, Hirschler (2, 3) presented evidence purporting to show that ion formation did indeed result from oxidation to triphenylcarbinol. This question was re-examined by Porter and Hall (4) who refuted this claim by demonstrating that the oxidation is photolytic; it could not have been responsible for the results of Hall and co-workers, although it might have been a factor in Hirschler's work. Since conclusive proof has been lacking, the authors maintained their respective positions in a later exchange (5, 6).

The fate of the H^- has now been ascer-

tained; the triphenylcarbonium ion results from the following Friedel-Crafts chemistry:



The pretreatments of catalyst and chemisorption procedures are detailed elsewhere (4). The procedures for qualitative and quantitative determination of benzene, diphenylmethane, and triphenylcarbinol were as follows: (1) The catalyst cell was placed on a vacuum line via a break-seal and the volatile benzene fraction was distilled into a trap at -195° . Benzene was identified by its PMR and its mass spectra. It was quantitatively determined by calibrated GLC and PMR. (2) The catalyst was transferred to a Soxhlet and extracted for several days with wet cyclohexane. The separation, identification, and quantitative determination of products were accomplished by GLC calibrated with authentic samples. The diphenylmethane fraction was purified by preparative GLC and its identity was confirmed by mass spectrography.

According to Eqs. (1) and (2), equimolar quantities of benzene, diphenylmethane, and triphenylcarbinol should be formed. The experimental results are summarized in Table 1, where this was established. The values for diphenylmethane and triphenyl-

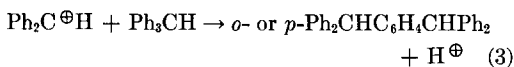
TABLE I
FRIEDEL-CRAFTS REACTION ON CRACKING CATALYSTS

Catalyst ^a	Pretreatment temperature (°C)	Number of experiments	Substrate	Available reagent (No./g × 10 ⁻¹⁹)	Reaction time ^b	Product (No./g × 10 ⁻¹⁸)			Recovery (%)
						Benzene	Ph ₂ CH ₂	Ph ₃ COH	
SA	550°	2	Ph ₃ CH	1.25	2 days	1.92	1.06	0.95	85
SA	550°	1	Ph ₃ CH	2.50	3 hours	—	0.82	0.76	95
SA	550°	2	Ph ₃ CH	2.50	2 days	2.35	1.48	1.02	91
SA	550°	1	Ph ₃ CH	12.5	2 days	—	3.5	3.2	96
HY	475°	2	Ph ₃ CH	2.50	6 days	0.17	0.37	0.32	—
HY	450°	1	Ph ₃ CH	25.0	3 days	—	2.74	2.58	99
HY	500°	1	Ph ₃ CH	25.0	4 days	—	1.98	1.66	89
						Benzene	PhCH ₃	C ₂₀ Compounds	
SA	550°	3	Ph ₂ CH ₂	2.5	3 days	15	0.7	3.0	
SA	550°	1	Ph ₂ CH ₂	3.75	6 days	21	0.6	3.0	
						PhOCH ₃ + PhOH	CH ₂ -C ₈ H ₄ OCH ₃	An ₂ CHOH	
SA	550°	1	An ₂ CH ₂	5.0	5 days	21	2.6	0.3	

^a SA is American Cyanamid silica-22.5%-alumina catalyst. Its surface area was 433 m²/g before pretreatment. HY was a decationated Linde Y-zeolite (66% Na⁺ removed; Lot No. 1280-133).

^b At 100°C.

carbinol were in good agreement with the carbonium ion concentration ($1.8 \times 10^{18}/\text{g}$) determined spectrophotometrically (4). The amount of benzene recovered was, however, somewhat higher. This could be explained by the following side reaction:



The presence of a small amount of α,α,α' -tetraphenylxylene was indeed detected in the GLC analysis. The amount of this by-product was found to depend on the length of heating at 100° .

That the formation of carbonium ion on the solid surface depends mainly, but not solely, on the stability of carbonium ion was demonstrated by studying the related chemistry of diphenylmethane and p,p' -dianisylmethane. With the less stable diphenylcarbonium ion, the catalyst remained white and no diphenylcarbinol (less than $\sim 10^{17}/\text{g}$) was detected. C_{20} compounds were found in about the expected amounts, indicating that the major reaction was arylation [Eq. (3)] and that hydride transfer [Eq. (2)] was unimportant. This was supported by the recovery of a larger quantity of benzene, than with triphenylmethane. Since the arylation reaction regenerates a proton, this reaction is not limited by the number of Bronsted sites on the catalyst. The C_{20} compounds were purified by GLC and identified by mass spectrography as the two isomers of α,α' -diphenylxylene. The same Friedel-Crafts reaction was also found with decationated Y-zeolite (Table 1).

When p,p' -dianisylmethane was chemisorbed, the presence of a small amount of p,p' -dianisylcarbonium ion was readily detected, in addition to the recovery of a large quantity of anisole and phenol. The p,p' -dianisylcarbonium ion is more stable than

diphenylcarbonium ion, but the presence of the methoxy group also activates the phenyl ring for substitution.

Leftin and Hall (1) reported that benzene was formed when triphenylmethane on silica-alumina was heated above 100° , but attached no significance to this, because they thought the carbonium ion concentration was tenfold higher than it is now known to be (3, 4). Since triphenylmethane does not appear to undergo hydride abstraction by Lewis sites, as previously supposed, convincing evidence for similar reactions with paraffin molecules is lacking and other routes to carbonium ions should be sought. In conclusion, Hirschler was correct in insisting that catalyst protons effected the formation of carbonium ions, but wrong concerning the mechanism. Hall and co-workers were incorrect in their suggestion that electrophilic centers were responsible, but correct in insisting that catalyst oxygen was not a factor.

This work was sponsored by the Gulf Research & Development Company as part of the research program of the Multiple Fellowship on Petroleum.

REFERENCES

1. LEFTIN, H. P., AND HALL, W. K., Actes Congr. Intern. Catalyse, 2^e, Paris, 1960 **1**, 1353 (1961).
2. HIRSCHLER, A. E., *J. Catalysis* **2**, 428 (1963).
3. HIRSCHLER, A. E., AND HUDSON, J. O., *J. Catalysis* **3**, 239 (1964).
4. PORTER, R. P., AND HALL, W. K., *J. Catalysis* **5**, 366 (1966).
5. HIRSCHLER, A. E., *J. Catalysis* **5**, 390 (1966).
6. HALL, W. K., AND PORTER, R. P., *J. Catalysis* **5**, 544 (1966).

CHING YONG WU
W. KEITH HALL

Mellon Institute
Pittsburgh,
Pennsylvania

Received June 20, 1967