cussions during the course of this work. They are also grateful to the Avco Manufacturing Corp., which kindly made time available on an IBM 650 MDDPM to perform the statistical analyses.

CINCINNATI 21, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OKLAHOMA STATE UNIVERSITY]

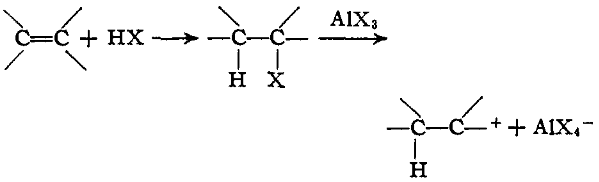
Kinetics of the Friedel–Crafts Ethylation of Benzene with Ethylene and with Ethylene-C^{14}

BY ERNEST M. HODNETT AND CHARLES F. FELDMAN, JR.[1]

RECEIVED AUGUST 8, 1958

A tenfold excess of benzene was alkylated with ethylene and aluminum bromide in a constant-volume recycle system. The over-all rate expression was found to be $-d[C_2H_4]/dt = k_2[C_2H_4][AlBr_3]$. When ethylene-$C^{14}$ was used, no change in specific radioactivity occurred during the reaction, indicating that the reaction of ethylene is fast and non-rate-determining.

Although the alkylation of benzene with ethylene has been known[2] since 1879 and has been used industrially for some years, the reaction mechanism has not been elucidated clearly. Kinetic data are sparse and not always reliable for this reaction, as for Friedel–Crafts alkylations in general. The reaction has been the subject of many reviews.[3] Thomas proposed a mechanism that involves the action of hydrogen chloride and aluminum chloride to form chloroaluminic acid, and the subsequent ionization of this acid. The proton so produced can attack any carbon–carbon double bond forming a carbonium ion which reacts further. However, Ulrich, Keutman and Geierhaus[4] presented evidence for the formation of an alkyl halide from the olefin and hydrogen halide, and its subsequent ionization by aluminum chloride to a carbonium ion. This mechanism indicates a similarity between Friedel–Crafts alkylations with olefins and those with alkyl halides.



$$>C=C< + HX \longrightarrow -\underset{H}{C}-\underset{X}{C}- \xrightarrow{AlX_3} -\underset{H}{C}-C^{+} + AlX_4^{-}$$

In order to understand the mechanism of alkylation of benzene with olefins, it is necessary to know: (1) the nature of the catalyst–olefin complex, (2) the contribution of a carbonium-ion process, and (3) the contribution of a displacement process. The kinetics of the ethylation of benzene using ethylene and ethylene-C^{14} under the catalytic influence of aluminum bromide have been determined in this investigation as a step toward a better understanding of the reaction.

Results and Discussion

The Reaction of Ethylene with Benzene.—The monoalkylation of benzene with ethylene using aluminum bromide as a catalyst was studied kinetically at approximately 100:10:1 ratios of benzene : ethylene : aluminum bromide. The excess benzene was used to make the reaction rate independent of its concentration and to minimize dialkylation. The reaction was homogeneous at the start, but became heterogeneous as a Friedel–Crafts oil was formed. When the data are plotted as ethylene pressure *versus* time, the curves are similar to those obtained by Jungk, Smoot and Brown[5] in alkylations of benzene with ethyl bromide using aluminum bromide as the catalyst.

The aluminum bromide catalyst was freshly distilled prior to each run and treated carefully to give as pure a catalyst as possible. However, the relative catalytic activity of the aluminum bromide from one run to another was not as constant as desired.

The reaction rates were followed by the uptake of ethylene at constant volume. Changing the rate of flow of ethylene through the reaction mixture had no effect on the reaction rate. Changes in the initial concentration of aluminum bromide resulted in changes of the specific rate constant k_1. When the first-order rate constants, k_1, are divided by the initial concentrations of the aluminum bromide, a second-order constant, k_2, is obtained which is fairly constant over the range of aluminum bromide concentrations used. The data for four runs are summarized in Table I.

The kinetic data for the first part of each run show a first-order dependence on ethylene pressure

$$-d[C_2H_4]/dt = k_1[C_2H_4]$$

However, since the rate constant, k_1, varies linearly also with the initial concentration of aluminum bromide, the rate expression must have the concentrations of both components to the first power.

$$-d[C_2H_4]/dt = k_2[C_2H_4][AlBr_3]$$

The tenfold excess of benzene in each case did not permit its detection in the rate expression.

The Alkylation of Benzene with Ethylene-C^{14}.—A kinetic isotope effect can be demonstrated by observing the change in the isotopic concentration

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[1] This investigation was supported by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-71, Project No. 5, and the Research Foundation of Oklahoma State University, and was conducted in the Radioisotopes and Radiations Laboratory. Presented at the 131st Meeting of the American Chemical Society, Miami, Fla., April, 1957. Abstracted from the Ph.D. dissertation of Charles F. Feldman, Jr.

[2] M. Balsohn, *Bull. soc. chim. France*, [2] **31**, 538 (1879).

[3] A. W. Francis, *Chem. Revs.*, **43**, 257 (1948); G. Baddeley, *Quart. Revs. (London)*, **8**, 355 (1954); C. C. Price in R. Adams, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, Chap. I; C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," American Chemical Society Monograph Series No. 87, Reinhold Publishing Corp., New York, N. Y., 1941.

[4] H. Ulrich, A. Keutman and A. Geierhaus, *Z. Elektrochem.*, **49**, 292 (1943).

[5] H. Jungk, C. R. Smoot and H. C. Brown, THIS JOURNAL, **78**, 2185 (1956).

TABLE I

RATE CONSTANTS FOR THE ALKYLATION OF BENZENE WITH ETHYLENE

Run	Reactants, moles/l. $AlBr_3$	C_2H_4	One cycle of Toepler pump, sec.	$k_1 \times 10^4$, sec.$^{-1}$	$k_2 \times 10^3$, l./mole sec.
3	0.060	1.473	20	0.87	1.45
4	.258	1.241	30	4.23	1.64
5	.139	1.314	30	1.66	1.19
8	.114	0.975	30	1.66	1.46

of a reactant.[6] This effect is found only when a bond to the isotopic atom is broken or formed in the rate-determining step of a reaction. To gain an insight into the nature of the ethylene–catalyst interaction and subsequent reactions, ethylene-C^{14} was used in the alkylation and the isotope effect was determined. Ethylene-C^{14}, 3.68 μc./mmole, was allowed to react with benzene under the catalytic influence of aluminum bromide. The reaction was studied by measuring the uptake of the gas at constant volume and the specific activity of the ethylene-C^{14} at various times. The results are summarized in Table II.

TABLE II

RADIOACTIVITY OF ETHYLENE-C^{14} DURING ALKYLATION

Ethylene reacted, %	Radioactivity, μc./mmole	Ethylene reacted, %	Radioactivity, μc./mmole
0.0	3.67	30.4	3.56
0.0	3.69	30.4	3.64
4.6	3.67	37.5	3.63
4.6	3.61	37.5	3.63
12.5	3.65		

The most common values[6] for the isotope effect of carbon-12 compared to carbon-14 are from 1.06 to 1.12 for k_{12}/k_{14}. The minimum detectable effect is about 1.01. Since the data in Table II show little, if any, change in the activity of the ethylene-C^{14} during the reaction, no kinetic isotope effect of ethylene is present in the reaction. The absence of any appreciable kinetic isotope effect indicates that the reaction of the ethylene is not a rate-determining step of the reaction. However, the observation of no isotope effect of ethylene does not eliminate the possible participation of the olefin–catalyst complex in a rate-determining step of the reaction.

Preparation of Ethylene-C^{14}.—This compound was prepared from barium carbonate-C^{14} obtained from Oak Ridge National Laboratory by the following series of reactions.

$$BaC^{14}O_3 + H_2SO_4 \longrightarrow C^{14}O_2 + BaSO_4 + H_2O$$

$$C^{14}O_2 + CH_3MgI \xrightarrow[\text{then } H_2O]{\text{dry ether}} CH_3C^{14}O_2H + Mg(OH)I$$

$$CH_3C^{14}O_2H + LiAlH_4 \xrightarrow[\text{then } H_2O]{\text{dry ether}} CH_3C^{14}H_2OH + LiAl(OH)_4$$

$$CH_3C^{14}H_2OH \xrightarrow[360\text{–}400^\circ]{Al_2O_3} CH_2{=}C^{14}H_2 + H_2O$$

The preparations of acetic acid-1-C^{14} and ethyl alcohol-1-C^{14}, and ethylene-C^{14} were based on published reports.[7–9] Weight and activity yields were good in most of the reactions. Later some ethylene-C^{14} was obtained from Isotope Specialties Co., Inc., Burbank, Calif.

Alkylations with Ethylene.—Alkylations were carried out in a glass reactor with a capacity of approximately 250 ml. The reactor was maintained at 9.2 ± 0.2° by passing cold water through a jacket surrounding it. Liquids could be added through a stopcock at the top and removed through a stopcock at the bottom. Gas entered the liquid reactant through a fritted disk; circulation of the gas was provided by a Toepler pump. Provision was made for taking small gaseous samples during the reaction.

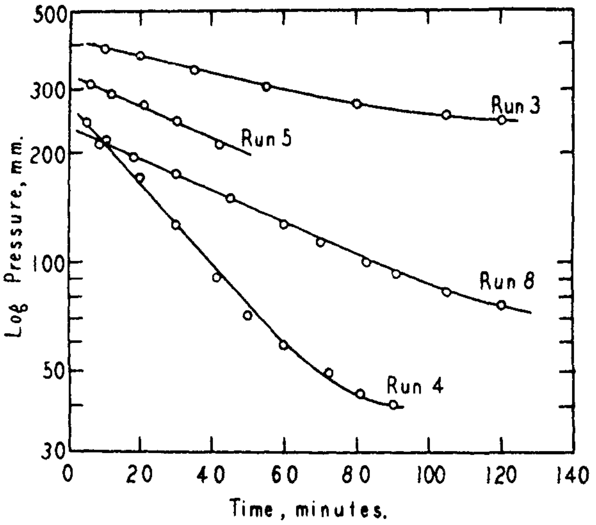

Fig. 1.—Change in pressure of ethylene during the alkylation of benzene.

Prior to the alkylation, aluminum bromide was distilled into a vial, which was capped and weighed. The catalyst was dissolved in a known amount of benzene (Merck benzene dried over calcium chloride, filtered, and distilled from sodium through a Snyder three-ball column, the first 20% of the distillate being discarded). A known amount of ethylene was condensed into a trap in the reaction system, and with the mercury in the Toepler pump in the down position, the pressure of ethylene in the reaction system was measured. The benzene–aluminum bromide solution was added to the reactor at time zero and the Toepler pump was placed in operation. Pressure readings were made at regular intervals when the pump was stopped with the mercury in the down position. About 15 seconds was required for the system to reach equilibrium for each reading.

TABLE III

ALKYLATION WITH ETHYLENE

Run 4; C_6H_6, 342.4 mmoles; C_2H_4, 37.8 mmoles; $AlBr_3$, 7.84 mmoles; 30-second cycles

Time, min.	Observed pressure, mm.	Observed pressure less 43.4, mm.
0	397.0	290.0[a]
5	298.0	245.6
10	261.0	217.6
20	214.5	171.1
30	168.5	125.1
41	133.5	90.1
50	115.0	71.6
60	103.0	59.6
72	93.0	49.6
81	87.0	43.6
90	84.0	40.6

[a] Extrapolated value.

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[6] G. A. Ropp, *Nucleonics*, **10**, No. 10, 22 (1952).

[7] M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert and P. F. Yankwich, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 178.

[8] R. M. Roberts, G. A. Ropp and O. K. Neville, THIS JOURNAL, **77**, 1764 (1955).

[9] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *ibid.*, **57**, 876 (1935).

Data for a typical run, no. 4, are given in Table III. The rapid drop in pressure during the first five minutes is attributed to the solution of ethylene in the reaction mixture. The vapor pressure of benzene at 9.2° was calculated to be 43.4 mm.[10]; this value was subtracted from the total pressure read. The amount of ethylene dissolved in the benzene could be calculated by assuming that Henry's law applies throughout the reaction. After the ethylene had been recycled for 5 minutes, the pressure drop was slow and steady. The pressure readings could then be extrapolated back to zero time in order to give the pressure which would have been read if the ethylene had not been in solution. The difference in the actual value and the extrapolated value would give the correction for the solubility of ethylene in the reaction mixture. Since this correction would be a constant fraction of the ethylene in a given reaction, it was not used in calculating the reaction rate constants.

When the logarithm of the pressure of the remaining ethylene is plotted against time, curves as shown in Fig. 1, for four runs are obtained. The slope of the initial part of each curve gives the value for the first-order reaction rate constant listed in Table I.

Radiocarbon Assay Method.—The ethylene-C^{14} was counted directly as the gas in an ionization chamber on an Applied Physics Corporation, model 30, vibrating reed electrometer. The apparatus used to prepare the samples for counting was one described by Wilzbach and Sykes[11] for assay of carbon-14 samples. The method was shown to give results that varied linearly over the small range of activities expected by making a series of dilutions of ethylene-C^{14}. Benzene and ethylbenzene were separated by condensation at −100° and 1 micron pressure: the amount of ethylene was determined in a constant-volume manometer. The assay was precise and accurate to ±1.0%.

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[10] T. E. Jordan, "Vapor Pressure of Organic Compounds," Interscience Publishers, Inc., New York, N. Y., 1954, p. 6.

[11] K. E. Wilzbach and W. Y. Sykes, *Science*, **120**, 484 (1954).

STILLWATER, OKLA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

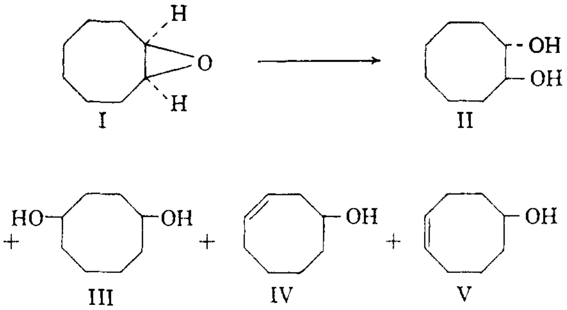
Proximity Effects. XVI. Solvolysis of cis-Cycloöctene Oxide with Various Acids[1,2]

BY ARTHUR C. COPE, J. MARTIN GRISAR AND PAUL E. PETERSON[3]

RECEIVED SEPTEMBER 2, 1958

The extent to which transannular reactions occur on solvolysis of *cis*-cycloöctene oxide with several acids has been determined. With trifluoroacetic acid, products of transannular reactions are formed exclusively; *i.e.*, *cis*-1,4-cycloöctanediol and 3- and 4-cycloöcten-1-ol. With acetic acid containing sodium acetate, the product contains 76% of the normal *trans*-1,2-cycloöctanediol and 24% of compounds formed by transannular reactions. Trichloroacetic acid, formic acid and acetic acid form mixtures of products formed by transannular reactions and normal solvolysis lying between these extremes, as shown in Table I.

The solvolysis of *cis*-cycloöctene oxide (I) with formic acid forms *trans*-1,2-cycloöctanediol (II), *cis*-1,4-cycloöctanediol (III) and 3- and 4-cycloocten-1-ol (IV, V).[4] While II represents the normal solvolysis product of an epoxide, compounds III, IV and V are formed by a "transannular reaction"[5] involving a shift of a hydrogen atom located in close spatial proximity to the epoxide function across the ring. Such hydrogen atoms are activated by a "proximity effect."[4a,6]



In the present work, the solvolysis of *cis*-cyclooctene oxide in trifluoroacetic acid, trichloroacetic acid, formic acid, acetic acid, acetic acid containing sodium acetate and trimethylacetic acid was investigated. The solvolyses were conducted by adding the oxide I to a tenfold molar excess of acid at a constant temperature. After completion of the reactions, the mixtures were neutralized and the esters formed were saponified with cold aqueous sodium hydroxide. The products were then examined by gas chromatography either before or after separation into two fractions by chromatography on alumina, one containing the glycols II and III and the other the unsaturated alcohols IV and V and several secondary products present in small amounts. The products were identified by gas chromatography, physical properties (including infrared spectra) and the preparation of crystalline derivatives, as described in the Experimental section and in Table II. The glycols II and III were separated by converting *trans*-1,2-cycloöctanediol into the isopropylidene ketal, followed by chromatography on alumina.[7] In each solvolysis gas chromatography was used to detect any *trans*-1,2-cycloöctanediol in the 1,4-glycol fraction, and in cases in which 1,2-glycol was present due to incomplete formation of the isopropylidene ketal, the ketalization procedure was repeated on the mother liquor from crystallization of III.

The allylic alcohol 2-cycloöcten-1-ol was shown by gas chromatography to be absent or present in small amounts in all of the solvolysis products. Secondary rearrangement products (Table II) were formed in the presence of the stronger acids, particularly trifluoroacetic acid, but their formation could be minimized by use of low reaction

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[1] Supported in part by a research grant (NSF-G5505) of the National Science Foundation.

[2] Paper XV, A. C. Cope and M. Brown, THIS JOURNAL, **80**, 2859 (1958).

[3] National Institutes of Health Postdoctoral Fellow, 1956–1958.

[4] (a) A. C. Cope, S. W. Fenton and C. F. Spencer, THIS JOURNAL, **74**, 5884 (1952); (b) A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons and G. W. Wood, *ibid.*, **79**, 3900 (1957).

[5] V. Prelog and K. Schenker, *Helv. Chim. Acta*, **35**, 2044 (1952).

[6] A. C. Cope, R. J. Cotter and G. G. Roller, THIS JOURNAL, **77**, 3590 (1955), and later papers in this series.

[7] A. C. Cope and G. W. Wood, *ibid.*, **79**, 3885 (1957).