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The overall protium–tritium kinetic isotope effect in the alcoholysis of tri-n-octylaluminum

In recent years a number of investigations have dealt with the determination of the kinetic isotope effect of hydrogen involving the cleavage of metal–carbon bonds. Protium–tritium isotope effects have been described involving reaction of Grignard reagents with alcohols, phenols, and water[1], and of deuterium in the methanolysis of several organometallic compounds[2]. A number of evaluations have been made of the protium–tritium effect in the cleavage of metal–carbon bonds in connection with studies on the mechanism of Ziegler or anionic polymerization[3,4,5], and the overall protium–tritium isotope effect has been determined in the alcoholysis of the reaction products of triethylaluminum with 1-octene[6].

We wish to report on a study carried out to evaluate this effect in the alcoholysis of an aluminum trialkyl, and on the variation of the effect with temperature. Values on temperature effects in the alcoholysis of aluminum alkyls have not been reported in the literature. Our results show that, particularly with isobutyl alcohol, the magnitude of the kinetic isotope effect varies markedly as the temperature is changed. The data suggest cautious use of kinetic isotope effect values, unless the experimental temperatures are well defined.

The alcoholyses were carried out at several temperatures with tri-n-octylaluminum and methanol or isobutyl alcohol containing a trace of tritium in the labile position. The hydrocarbon product was isolated, radioassayed, and the overall kinetic isotope effect, $\overline{k_H/k_T}$, was determined from a comparison with the radioassay of the alcohol used. The results are summarized in Table 1; Arrhenius-type plots of $\overline{k_H/k_T}$ are shown in Fig. 1.

The alcoholysis may be depicted stepwise as

$$R_3Al + R'OH \rightarrow R_2AlOR' + RH \qquad (1)$$

$$R_2AlOR' + R'OH \rightarrow RAl(OR')_2 + RH \qquad (2)$$

$$RAl(OR')_2 + R'OH \rightarrow Al(OR')_3 + RH \qquad (3)$$

with complexing also occurring between the various aluminum compounds as well as with unreacted alcohol. Experiments carried out with stoichiometric amounts of alcohol indicate that reaction (3) is considerably slower than reactiốn (1) and probably slower than reaction (2). When such stoichiometric reactions were carried out at room temperature, only 56% of the theoretical radioactivity was found in the hydro-

TABLE 1

OVERALL KINETIC ISOTOPE EFFECT IN THE REACTION OF TRI-n-OCTYLALUMINUM WITH TRITIUM-TAGGED METHANOL AND ISOBUTYL ALCOHOL IN n-HEXANE

Temperature	*Isotope effect,* $\overline{k_H/k_T}$		
(°C)	*Methanol*	*Isobutyl alcohol*	
0	2.87	7.82	
0	2.94	7.17	
26		4.8	
46	2.31		
46	2.32		
46	2.31		
68		2.73	2.78 ± 0.08(2)
68		2.78	
68		2.85	
68		2.73	
68		2.78	
68		2.79	
104[a]		1.76	
ΔE^a(kcal/mole)	−0.8	−2.8	

[a] Solvent was n-nonane.

carbon product, but when performed at elevated temperatures, nearly the theoretical radioactivity was obtained.

The temperature dependence of the isotope effect is expressed as ΔE^a in Table 1 and represents the difference, $E_H^a - E_T^a$, between the activation energies of the

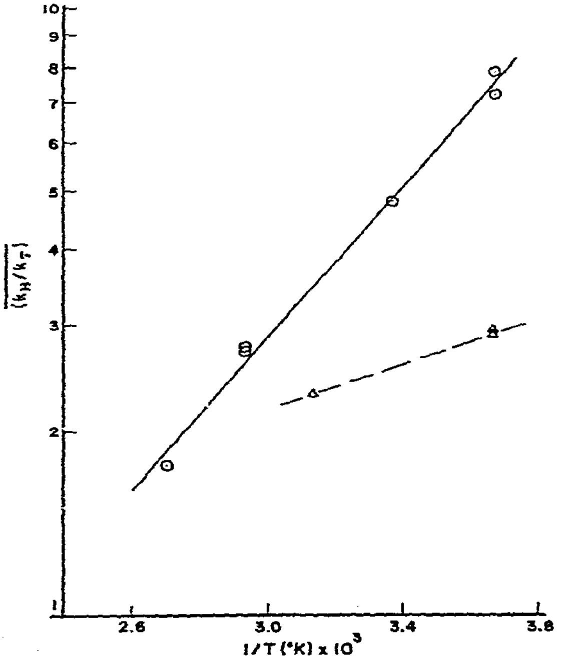

Fig. 1. Arrhenius plot of the temperature dependence of the overall isotope effect in the alcoholysis of tri-n-octylaluminum. — — methanol, $\Delta E^a = -0.8$ kcal/mole; —— isobutyl alcohol, $\Delta E^a = -2.8$ kcal/mole.

protium and tritium species. Since the data reported here are the arithmetic averages of isotope effects which stem from reactions (1), (2), and (3), no direct information regarding the rate-determining step[7] can be gained from these data. The evidence for the slow nature of reaction (3), and the much larger temperature dependence observed with isobutyl alcohol than with methanol, however, lead us to believe that (3) is responsible for the major part of the observed isotope effect. Particularly in the case of isobutyl alcohol steric requirements in the transition state of reaction (3), which presumably increase the distance of nearest approach between alcoholic hydrogen and reactive carbon, should lead to a greater isotope effect. In this connection, Assarsson[1] has reported an isotope effect of 1.06 with methylmagnesium iodide and methanol at 20°, and one of 3.7 with this Grignard reagent and 2,6-di-tert-butyl-4-methylphenol.

The individual determination of the isotope effect for reactions (1), (2), and (3) should be possible by suitable alcoholysis experiments with the alkoxide products from reaction (1) and (2) and knowledge of the overall isotope effect. Such experiments are planned and are expected to yield information on the respective transition states, and thus on the mechanism of alcoholysis.

Experimental

Materials. Dry methanol and isobutyl alcohol were treated with a trace of tritium-enriched water and were then passed through activated, type 4A Molecular Sieves (The Linde Co.). Final specific activity was approximately 10^6 disintegrations per second/mole; water content was less than 50 ppm by titration with Karl Fischer reagent. Tri-n-octylaluminum (Texas Alkyls) was diluted with an equal volume of the appropriate solvent and used as such. Analysis of the hydrolysis products by infrared, gas chromatography, and mass spectrometry gave the following composition in wt. %: 65% C_8 n-paraffin, 12% C_4 parraffin, 1% C_8 alcohol, 15% C_{16} olefin, 7% C_{16} paraffin. Tri-n-ethylhexyl aluminum was prepared according to Ziegler[8]. n-Hexane and n-nonane were dried by passage through activated, type 4A Molecular Sieves.

Procedure. Radioassays were carried out in a Packard Instrument Co. Tri-Carb liquid scintillation counter. Glass vials of 20 ml capacity were filled with 15 ml of phosphor solution, containing 3.0 g 2,5-diphenyloxazole, (PPO), and 0.1 g *p*-bis-[2-(5-phenyloxazolyl)] benzene, (POPOP), in one liter of dry technical grade xylene, and 0.5 ml of sample was added. Ten or more successive 10-second counts were averaged, the total disintegrations counted never being less than 10^5. The counting error was less than 2% and the efficiency was approximately 16%. Quenching effects were negligible. The isotope effect, $\overline{k_H/k_T}$, was calculated as the molar activity ratio of alcohol to octane.

In a typical determination of the isotope effect, 20 ml of a 50 vol. % solution of tri-n-octylaluminum in hexane were added dropwise to 40 ml (10-fold excess) of radiotagged methanol in a magnetically stirred flask. The temperature of the mixture was controlled by an outside bath and the addition was carried out under a blanket of dry, oxygen-free nitrogen. After completion of the addition, which required about 30 min, the mixture was stirred for another hour, washed with dilute acid and base, and finally several times with water. The hydrocarbon layer was fractionated in a 30-cm helices-packed column, and the cut boiling between 123° and 126° was used for radioassay (>99% octane by gas chromatography). Completeness of the alcoholysis was checked by performing a similar experiment with untagged alcohol, introducing radiotagged alcohol after the hour long stirring period, and allowing the mixture to react for an additional 16 hours. Radioassay of product octane indicated that the reaction with the tagged alcohol was less than 1%.

Alcoholysis experiments were also performed in which a stoichiometric amount of the alcohol was added dropwise to a solution of the aluminum alkyl in hexane, using an apparatus as described above. In three such experiments performed with isobutyl alcohol at 0° the observed radioactivity of the octane was 56 ± 1% of that calculated. With methanol at 50° the activity was 86% of the expected. A similar experiment performed with tris(2-ethylhexyl)aluminum at 70° gave octane with 99% of the calculated activity.

Research Department,
Monsanto Company,
Texas City, Texas (U.S.A.)

ERWIN KOHN*
JACK M. GILL**

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* Present address: Chemistry Department, Southwestern State College, Weatherford, Okla, 73096 (U.S.A.)
** Present address: Research and Engineering Department, Varian-Aerograph, Walnut Creek, Calif. (U.S.A.)

Kinetics of tin–phenyl cleavage by 8-quinolinol under ansolvous conditions

Recently, the kinetics of the formation of compounds of the type X_2SnOx_2, where X = Cl, Br, Ox = 8-quinolinolate, were studied using dimethyl sulfoxide solutions[1].

$$(C_6H_5)_2SnX_2 + 2\,HOx \rightarrow X_2SnOx_2 + 2\,C_6H_6 \qquad (1)$$

The rate of formation of product obeys a pseudo-first-order law and the observed rate constants, k_ψ, vary as a function of the concentration of 8-quinolinol. The appropriate rate expression is:

$$\text{rate} = k_\psi[(C_6H_5)_2SnCl_2] = (k_1 + k_2[HOx]^2)\,[(C_6H_5)_2SnCl_2]$$

Evidence has been presented[1] that the two-term rate expression reflects two cleavage