dium catalyst on charcoal is given by curve B of Figure 1. Rapid conversion is now initiated at a lower temperature with a peak resulting at 290°.

The thermograms were analyzed using the method of Piloyan, *et al.*,[7] and gave an activation energy of 46 ± 2 kcal/mole for the uncatalyzed sample. This is in good accord with the value of 42.8 kcal/mole reported by Kistiakowsky and Smith.[1] The palladium-catalyzed samples gave values of activation energy of 28 ± 1.6 kcal/mole in agreement with the acceleration of the reaction by palladium reported by Urushibara and Simamura.[3]

We are presently investigating several areas closely related to the stilbene case. These include the effect of aromatic substituents on the kinetic parameters and more general structure–reactivity relationships of these systems. The results of this work will appear in a future paper.

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Homogeneous Metal-Catalyzed Exchange of Aromatic Compounds. A New General Isotopic Hydrogen Labeling Procedure

Sir:

We wish to report a simple one-step procedure for the exchange of hydrogen in isotopic water with a large number of aromatic compounds in the presence of *homogeneous* metal catalysts such as platinum(II) salts. The results of this work are of importance to fundamental catalysis since the present system constitutes the *homogeneous* analog of the conventional *heterogeneous* method which utilizes prereduced group VIII transition metals as catalysts, platinum being the most active.[1] A possible relationship between the two systems would thus support the concept that the chemistry of adsorbed molecules and the chemistry of inorganic coordination compounds are intimately related,[2] presumably through π-complex formation.

In addition to the catalytic implications of the present technique, the procedure constitutes a new, rapid, one-step method for labeling a large range of organic compounds with deuterium and/or tritium. It possesses a number of distinct advantages when compared with conventional procedures such as Wilzbach gas irradiation for tritium[3] and heterogeneous exchange in solution, which is applicable to both hydrogen isotopes.[1b]

In a typical procedure using the reagent quantities shown in Table I, a solution of acetic acid, heavy water, hydrochloric acid, the organic compound, and disodium platinum tetrachloride as catalyst is allowed to react in an evacuated sealed tube at a temperature within the range 25–120°, this being determined by the isotope used and the enrichment required. All examples reported in the table utilize deuterium as the source of isotope since low-voltage mass spectrometry and nmr readily yield total isotope incorporation and orientation without the extensive chemical degradation necessitated by tritium. Acetic acid is essential to the medium to ensure homogeneity of phase. The acidity of the solution is critical, since this should be high enough to stabilize the catalyst complex against reduction and thus prevent precipitation of platinum. However, the acidity should not be too high, otherwise the *homogeneous* metal-catalyzed process is inhibited and only acid exchange occurs in those compounds where this is possible. If platinum does precipitate from the reaction mixture it is found that the inorganic acid present poisons subsequent *heterogeneous* exchange on the surface of the precipitated catalyst. With certain compounds, such as mesitylene, where the ring hydrogens readily exchange under acid conditions, it is possible to label both methyl and ring hydrogens in the molecule in one step by effecting a compromise in acidity such that both metal- and acid-catalyzed isotope incorpora-

Table I. Homogeneous Metal-Catalyzed Deuteration of Selected Aromatics

Compound	Weight, g	Media for exchange[a]	Temp, °C	Exchange time, hr	Deuterium distribution, %							% deuteration
					D_0	D_1	D_2	D_3	D_4	D_5	D_6	
Benzene	0.176	A	82	4	82.2	2.6	2.8	2.9	3.1	3.5	2.9	10.7[b]
Fluorobenzene	0.205	A	82	4	87.6	3.1	3.6	4.0	1.5	0.2		5.9
Chlorobenzene	0.221	A	82	4	87.1	3.0	3.7	6.0				5.7
Toluene	0.173	A	82	4	84.6	4.1	4.4	4.8	1.1	0.7	0.4	4.7
t-Butylbenzene	0.173	A	82	4	87.6	3.1	4.4	5.0				5.4[d]
Trifluorotoluene	0.238	A	80	3	92.8	1.35	1.95	3.85				3.4
Benzene	0.088	B	75	2.3	87.8	1.65	1.65	1.85	2.05	2.40	2.70	7.8[c]
Diphenyl	0.100	B	75	2.3	83.0	3.0	4.0	5.5	1.7	1.3	1.5	5.0
Dibenzyl	0.100	B	75	2.3	83.5	3.8	4.6	5.5	1.1	0.7	0.5	3.1
Naphthalene	0.100	B	75	2.3	75.3	20.4	3.3	0.6				3.6
Phenanthrene	0.100	B	75	0.85	80.7	16.2	1.4	0.25				2.0
Pyrene	0.050	B	75	0.7	85.4	13.7	1.0					1.57

[a] 2.0 ml of exchange media was used in each run. Solution A: CH_3COOD (1.00 mole), D_2O (1.00 mole), K_2PtCl_4 (1.48×10^{-3} mole), and DCl (1.48×10^{-3} mole); solution B: CH_3COOD (1.00 mole), D_2O (0.50 mole), Na_2PtCl_4 (1.30×10^{-3} mole), and DCl (1.30×10^{-3} mole). [b] Theoretical equilibrium for benzene, 85.7%. [c] 82.1%. [d] Calculated assuming exchange in the aromatic portions only.

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(1) (a) Part XXXVII of a series entitled "Catalytic Deuterium Exchange Reactions of Organics." Part XXXVI: G. E. Calf, B. D. Fisher, and J. L. Garnett, *Australian J. Chem.*, in press. (b) J. L. Garnett and W. A. Sollich-Baumgartner, *Advan. Catalysis*, **16**, 95 (1966).

(2) M. Orchin, *ibid.*, **16**, 1 (1966).

(3) K. E. Wilzbach, *J. Am. Chem. Soc.*, **79**, 1013 (1957).

tion occur, although the efficiency of the two processes is reduced under these conditions.

In the very large number of compounds that have been examined by the present technique, aromatics are generally quite reactive whereas aliphatics such as cyclohexane exchange very slowly. A representative number of compounds is included in Table I to illustrate the type of reactivity to be expected, the data being reported in such a manner as to indicate relative rates of reaction; thus relatively low exchange temperatures are shown together with low deuteration. If the temperature is raised to 100–110° and the time of exchange increased slightly, equilibrium isotope incorporation is readily achieved in the active aromatic hydrogen positions of all compounds listed. A comparison of the rates of exchange of toluene and chlorobenzene (Table I) shows conclusively that the reaction is not acid catalyzed. The degree of exchange is not markedly influenced by the electronic character of the substituent (toluene *vs.* trifluorotoluene). This conclusion is further supported by the isotope orientation in chlorobenzene, *t*-butylbenzene, and trifluorotoluene where the exchange is exclusively *meta* and *para*, as indicated by both the cutoff in the low-voltage mass spectrum and nmr data. For many of the monosubstituted benzenes, there is a remarkable similarity in isotope orientation between the present homogeneous platinum(II) system and heterogeneous platinum-catalyzed exchange.[4] For certain other compounds there are significant differences in exchange properties from the two procedures; thus as a potential isotopic hydrogen labeling tool it is predicted that the homogeneous technique will replace heterogeneous methods for many compounds and also act as a complementary procedure for the labeling of many others. A detailed summary of the advantages of the present procedure together with a discussion of the mechanistic implication of the work with respect to fundamental catalysis will be published in a series of papers elsewhere.

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Contact and Solvent-Separated Ion Pairs of Carbanions. IV. Specific Solvation of Alkali Ions by Polyglycol Dimethyl Ethers

Sir:

We recently reported that variations in temperature and solvent composition caused reversible changes in the ultraviolet and visible absorption spectra of solutions of carbanions and radical anions.[1] The changes, showing distinctly separate absorption maxima (particularly pronounced with fluorenyl salts), were attributed to the existence of a rapid equilibrium between contact or intimate ion pairs (C^-,M^+) and solvent-separated ion pairs $(C^-\|M^+)$. The ratio of the fractions of the two kinds of ion pairs was found to be a sensitive function of the basicity and geometrical structure of the solvating molecules.

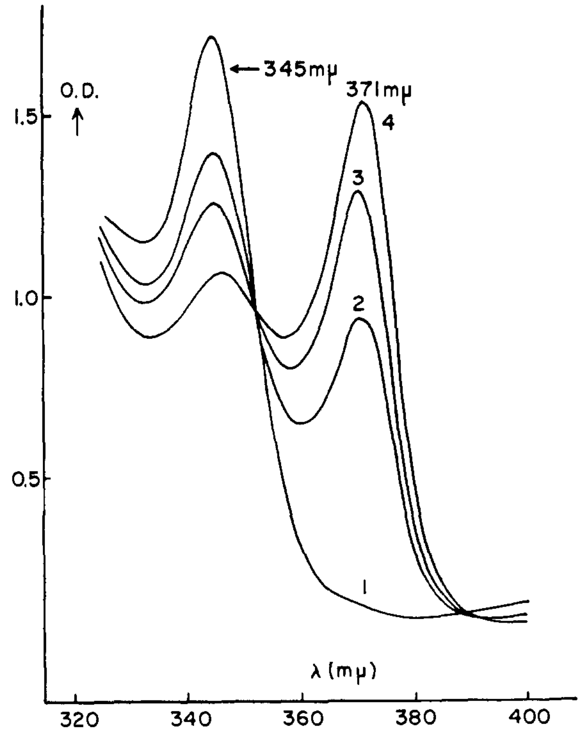

Figure 1. Spectrum of F^-,Li^+ in mixtures of dioxane and $CH_3O(CH_2CH_2O)_3CH_3$; $[F^-,Li^+] \approx 1.4 \times 10^{-3}$ *M*. Curve 1: pure dioxane; curves 2, 3, and 4 represent solutions with [PGDE] = 6.46×10^{-3} *M*, 11.3×10^{-3} *M*, and 24.3×10^{-3} *M*, respectively.

We have now investigated a series of polyglycol dimethyl ethers (PGDE) of the formula $CH_3O(CH_2CH_2O)_xCH_3$ with respect to their behavior in solvating alkali cations. These molecules are expected to be powerful solvating agents because of the presence of multiple coordination sites within the same molecule.[2,3] In our experiments, a solution of fluorenyllithium in dioxane (only contact ion pairs are observed in this solvent) was titrated under vacuum with a solution of the same salt in a mixture of dioxane and the respective polyglycol ether. The latter mixture was prepared so as to contain close to 100% solvent separated ion pairs. After each addition the optical spectrum was recorded. (With fluorenylsodium, some difficulties were encountered with dioxane as solvent, and THF was therefore used.)

An example involving triethylene glycol dimethyl ether is shown in Figure 1. The appearance of an isosbestic point confirms the stoichiometry of the reaction. The ratio of the fraction of the solvent-separated ion pair (371 mμ) over that of the contact ion pair (345 mμ) can be determined since the "pure" ion-pair spectra are known. Let us denote by *n* the number of PGDE mole-

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