couplings has been discussed in detail elsewhere.[10] The signs of the two fluorine–fluorine couplings above have also been related directly to proton–proton couplings.[11] The P–C–F coupling was common to many of the fluorophosphine derivatives. The absolute signs given in Table I were in some cases based on the positive sign for this coupling. A careful scrutiny of the changes of the magnitude of the P–C–F coupling with the nature of the substituents in phosphines strongly suggests that no inversion of the sign of this coupling is likely for known fluorophosphines.[12] The P–F coupling is negative which is similar to the sign of the directly bonded Si–F coupling.[13,14] The results for CF_3P^{-}–$P^{+}(CH_3)_3$ and $(CF_3)_2P$–$P(CH_3)_2$ establish that the directly bonded P–P coupling constant is negative even between phosphorus nuclei of significantly different valences.[15] The F–C–P–F coupling is negative as is the analogous F–C–C–F coupling. The signs found in this study suggest that ^{31}P in general participates electronically in coupling to ^{19}F in a manner reminiscent to that of ^{1}H. Phosphorus appears to play a role similar to a carbon atom in a series of atoms in the bonding fragment between coupled nuclei.

[10] S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Am. Chem. Soc.*, **88**, 2689 (1966).

[11] (a) M. Barfield and J. D. Baldeschwieler, *J. Mol. Spectry.*, **12**, 23 (1964); (b) D. F. Evans, S. L. Manatt, and D. D. Elleman, *J. Am. Chem. Soc.*, **85**, 238 (1963); (c) S. L. Manatt and D. D. Elleman, unpublished work.

[12] Details to be discussed elsewhere.

[13] S. S. Danyluk, *J. Am. Chem. Soc.*, **86**, 4504 (1964).

[14] The signs of the couplings which we refer to in this work are those for the so-called reduced coupling defined as $K_{ij} = (2\pi/\hbar\gamma_i\gamma_j)J_{ij}$. This parameter is independent of nuclear properties and reflects directly the magnitude of electronic interactions. In the case of ^{29}Si, $\gamma_{^{29}Si}$ is negative so although J_{Si-F} is positive, K_{Si-F} is negative.

[15] In support of the results presented here R. K. Harris (private communication) has recently found in double-resonance experiments on $(CH_3)_2P$–$P(CH_3)_2$ that the P–P coupling is negative relative to the directly bonded C–H coupling.

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Kinetics of *cis–trans* Isomerizations by Differential Thermal Analysis

Sir:

In the course of other investigations utilizing differential thermal analysis, we became aware of the potentialities of this technique for the determination of the kinetics and energetics of thermally induced reactions such as *cis–trans* isomerizations. We have focused our initial attention on the *cis*-to-*trans* isomerization of stilbene because this system has been extensively studied.[1-3]

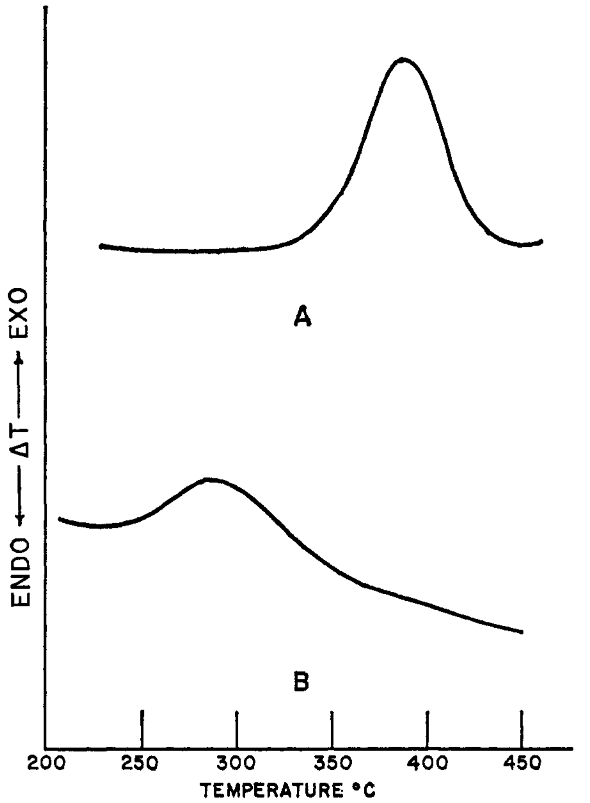

Figure 1. Thermograms for stilbene (A) and for stilbene with 10% palladium on charcoal as a catalyst (B).

While the technique of differential thermal analysis is not new, recent advances in instrumentation have greatly increased the sensitivity and reliability of the method. Review articles have discussed the instrumentation and the application of the method to inorganic, organic, and polymer systems.[4]

A number of papers have appeared which discuss the application of differential thermal analysis to the determination of kinetic parameters.[5-7] We have used the method of Piloyan, *et al.*,[7] to determine the activation energy of the spontaneous *cis*-to-*trans* isomerization of stilbene.

Whereas rate parameters are normally determined at a constant temperature, in differential thermal analysis the temperature is increased at a constant rate until eventually the equilibrium state is reached. Conversion occurs over a temperature range rather than at one temperature. Plot A of Figure 1 shows the thermogram obtained with *cis*-stilbene in a sealed cell using the Du Pont Model 900 differential thermal analyzer. Conversion to the *trans* form occurs rapidly and spontaneously once a temperature of about 300° is reached. The peak in the thermogram occurs at 385°, and the reaction is essentially completed at 440°. Only solid material could be isolated from the reaction product. This melted at 124°, the melting point of *trans*-stilbene.

The thermogram obtained when *cis*-stilbene is heated in a closed system with an equal quantity of 10% palla-

[1] G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.*, **56**, 638 (1934).

[2] T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938).

[3] Y. Urushibara and O. Simamura, *Bull. Chem. Soc. Japan*, **14**, 323 (1939).

[4] C. B. Murphy, *Anal. Chem.*, **34**, 298R (1962); **36**, 347R (1964); **38**, 443R (1966).

[5] H. J. Borchardt and F. Daniels, *J. Am. Chem. Soc.*, 79, 41 (1957).

[6] H. E. Kissinger, *J. Res. Natl. Bur. Std.*, **57**, 217 (1956).

[7] G. O. Piloyan, I. D. Ryabchikov, O. S. Novikova, *Nature*, **212**, 1229 (1966).

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.

Table I. Homogeneous Metal-Catalyzed Deuteration of Selected Aromatics

Compound	Weight, g	Media for exchange[a]	Temp, °C	Exchange time, hr	Deuterium distribution, % D_0	D_1	D_2	D_3	D_4	D_5	D_6	% deuteration
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.

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-

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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).