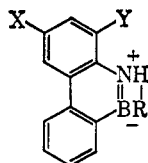


good test of chemical theories. We wish to report the first quantitative measurement of reactivity of such a boron-containing aromatic in a typical chemical reaction, *i.e.*, the partial rate factor (PRF) for nitration of 10,9-borazarophenanthrene (Ia) in acetic anhydride at 0°.

Previous studies<sup>3</sup> had shown that Ia gives a mixture of the 6- (Ib) and 8-nitro (Ic) derivatives under these conditions, together with 8-nitro-10-hydroxy-10,9-bor-



- Ia, R = CH<sub>3</sub>; X = Y = H  
 b, R = CH<sub>3</sub>; X = NO<sub>2</sub>; Y = H  
 c, R = CH<sub>3</sub>; X = H; Y = NO<sub>2</sub>  
 d, R = OH; X = H; Y = NO<sub>2</sub>

azarophenanthrene (Id) formed<sup>3</sup> by secondary oxidation of Ic. Preliminary trials showed Ia to be comparable in reactivity with perylene, a hydrocarbon which gives almost exclusively the 3-nitro derivative on nitration in acetic anhydride at 0° with a partial rate factor of 77,000.<sup>4</sup> It was also established that nitration of a mixture of Ia and perylene, if carried to low conversions at 0°, gave only Ib, Ic, and 3-nitroperylene, formation of Id being avoided.

The nitration product was analyzed by the spectrophotometric procedure of Dewar and Urch,<sup>5</sup> this has been greatly improved in these laboratories by Mr. J. Hashmall, who has written a computer program able to handle multicomponent mixtures to replace the original graphical procedure. Two independent and concordant measurements led to the following PRF's for formation of Ib and Ic: Ib, 937,000; Ic, 2,060,000.

Ia is thus a very reactive ring system; the PRF's for the corresponding positions in phenanthrene are:<sup>4</sup> 3 position, 300; 1 position, 360. The values for Ia are also of general interest in that they are the largest yet reported for nitration in acetic anhydride, and show that such reactions are not diffusion controlled below rates corresponding to partial rate factors of at least  $2 \times 10^6$ .

No quantitative calculations of PRF's are available as yet, due to the lack of information concerning parameters for boron; indeed, the value of measurements such as these lies largely in the assistance they may give to attempts to extend existing semiempirical MO treatments. For example, the localization energies predicted<sup>3</sup> by the simple PMO method are: 6 position,  $2.60\beta \times 1.67A$ ; 8 position,  $2.32\beta + 1.38A$ , where

$$A = (\alpha_B - \alpha_C)(\alpha_N - \alpha_C)^{-1}$$

If we assume that carbon is half way between boron and nitrogen in electronegativity, so that  $A = 1$ , and use the relation between PMO localization energies and PRF's established<sup>4</sup> for hydrocarbons, we find the values predicted for Ia to be: 6 position, 5,100,000; 8 position, 4,550,000. However, published data for valence state ionization potentials, etc.,<sup>6</sup> suggest that carbon is some-

what nearer to boron than to nitrogen in electronegativity, so that  $A < 1$ ; setting  $A = 0.9$  gives predicted PRF's of 903,000 and 1,130,000, respectively, in very reasonable agreement with experiment.

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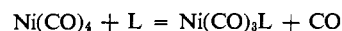
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## Nickel Tetracarbonyl. The Mechanism of Nucleophilic Substitution

Sir:

In an earlier communication<sup>1</sup> it was stated that the carbon monoxide exchange reaction ( $L = {}^{14}\text{CO}$ )<sup>2,3</sup> of  $\text{Ni}(\text{CO})_4$  appeared to occur by a different mechanism



from other substitution reactions ( $L = \text{R}_3\text{P}$ ,  $\text{RNC}$ ,  $(\text{RO})_3\text{P}$ ).<sup>1,3,4</sup> We have remeasured the rates of these reactions. We do not confirm previous results for the CO exchange, but for ligand substitution our results fall between previous values determined in similar solvents. We now conclude that all substitutions, including exchange, proceed by the same mechanism.

In all the previous cases, a first-order rate law was observed; *i.e.*, the reaction rate was independent of the concentration of nucleophile. All nucleophiles, except CO, reacted at approximately equal rates. At 25°, the rates of CO exchange (studied using <sup>14</sup>CO and measuring radioactivity) and ligand substitution (studied by CO evolution<sup>3</sup> or infrared spectrophotometry<sup>4</sup>) were approximately equal. At lower temperatures, ligand substitution became relatively the slower process. The activation parameters for <sup>14</sup>CO exchange and triphenylphosphine ( $\text{Ph}_3\text{P}$ ) substitution, obtained for reaction in heptane, were respectively:  $\Delta H^\ddagger = 10$  and 21 kcal mole<sup>-1</sup>;  $\Delta S^\ddagger = -36$  and 1 eu.

These observations have led to speculation about the reaction mechanisms.<sup>1,3,5</sup> It was argued that, although the rate-determining step in each case must involve only  $\text{Ni}(\text{CO})_4$ , the same activated complex could not be involved in both CO exchange and ligand substitution since the activation energies are radically different.

We have redetermined the rates of CO exchange and  $\text{Ph}_3\text{P}$  substitution, in hexane solvent, from 0 to 30°. The system is arranged so that no gas phase is present. In Table I, our rates and activation parameters are compared and are essentially the same for the two reactions.

In our experiments, <sup>18</sup>O was allowed to react with  $\text{Ni}(\text{C}^{16}\text{O})_4$ , and the concentrations of the five species  $\text{Ni}(\text{C}^{16}\text{O})_n(\text{C}^{18}\text{O})_{4-n}$  ( $n = 0-4$ ) were followed by infrared spectrophotometry. We confirm the first-order rate law, and detailed analysis of the concentration changes for the species  $\text{Ni}(\text{C}^{16}\text{O})_4$  and  $\text{Ni}(\text{C}^{16}\text{O})_3(\text{C}^{18}\text{O})$  gave the rate constants (a discussion of the spectra of the

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(5) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 543.

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**Table I.** Rate Constants<sup>a</sup> and Activation Parameters<sup>b</sup> for the Reaction of Ni(C<sup>16</sup>O)<sub>4</sub> with C<sup>18</sup>O and Ph<sub>3</sub>P in Hexane Solution

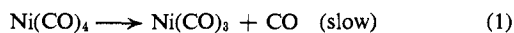
Temp, °C	Rate constant: 10 <sup>4</sup> k sec <sup>-1</sup>	
	C <sup>18</sup> O exchange <sup>c</sup>	Ph <sub>3</sub> P substitution <sup>d</sup>
0.5	2.50	2.45
10.0	12.5	11.0
20.0	52.0	49.8
30.0	210	206
ΔH‡, kcal mole <sup>-1</sup>	24.3 ± 0.4	24.2 ± 0.2
ΔS‡, eu	14 ± 2	13 ± 1

<sup>a</sup> First-order rate law. <sup>b</sup> Errors given represent probable error estimated from experimental errors. <sup>c</sup> Standard deviation, 2%. <sup>d</sup> Standard deviation, 1%.

five species will be published separately). The Ph<sub>3</sub>P substitution reactions were also followed by infrared spectrophotometry, and also obey a first-order rate law.

In competition experiments in which C<sup>18</sup>O and Ph<sub>3</sub>P were allowed to react simultaneously with Ni(C<sup>16</sup>O)<sub>4</sub>, both Ni(C<sup>16</sup>O)<sub>3</sub>(C<sup>18</sup>O) and Ni(C<sup>16</sup>O)<sub>3</sub>(Ph<sub>3</sub>P) formed more slowly than in the single-ligand experiments at the same temperature. However, the sum of their rates of formation, which was equal to the rate of reaction of Ni(C<sup>16</sup>O)<sub>4</sub>, was approximately equal to the rate of either of the single-ligand reactions. With equimolar quantities of C<sup>18</sup>O and Ph<sub>3</sub>P, the latter reacted about five times as fast. A tenfold excess of Ph<sub>3</sub>P over C<sup>18</sup>O virtually eliminated the exchange reaction.

We conclude, therefore, that the description of the reaction mechanism requires at least two steps. The first, which is rate determining, does not involve the reacting nucleophile and is the same for CO exchange and Ph<sub>3</sub>P substitution. This is followed by rapid reaction of the nucleophile with the reactive intermediate formed in step 1. It seems likely that the reactive intermediate is the species Ni(CO)<sub>3</sub>, e.g.



We have also studied the gas-phase exchange reaction (Ni(C<sup>18</sup>O)<sub>4</sub>-C<sup>16</sup>O) and find it to be first order in Ni(CO)<sub>4</sub> and zero order in CO. The rate constants are about three times greater than in hexane solution, and the activation energies are very similar in the gas phase and in hexane. This creates a conflict with the postulated<sup>6</sup> mechanism for Ni(CO)<sub>4</sub> decomposition in the gas phase, where step 1 is also supposed to be rate controlling, at low CO pressure, but is about 1% of the rate of CO exchange. We are studying the gas-phase thermal decomposition reaction further to resolve this conflict.

**Results from Previous CO Exchange.** We have considered possible sources of error in the original <sup>14</sup>CO-exchange experiments. In these, a mixture of <sup>12</sup>CO and <sup>14</sup>CO was pumped through a solution of Ni(<sup>12</sup>CO)<sub>4</sub>, and the reaction was assumed to occur in, and at the temperature of, the solution. The radioactivity of a substantial gas phase (at laboratory temperature) was measured. It is now clear that some exchange always occurred in the gas phase, because of the volatility of Ni(CO)<sub>4</sub>. Approximate calculations, using measured values of the vapor pressure of Ni(CO)<sub>4</sub> over solutions, show that up to 50% of the observed exchange could have occurred in the gas phase in the most unfavorable case. This effect would be greatest at the lowest solution

(6) R. K. Chan and R. McIntosh, *Can. J. Chem.*, **40**, 845 (1962).

temperature and would result in an "observed" activation energy much lower than the "true" activation energy. If we take our present (infrared) results to be correct, then the deviation of the previous results can be understood. Exchange studies by the <sup>14</sup>CO method for other volatile metal carbonyls such as CoNO(CO)<sub>3</sub> may also be in error due to gas-phase reaction.<sup>7</sup>

**Acknowledgment.** The work done at Northwestern was supported in part by a National Science Foundation Grant.

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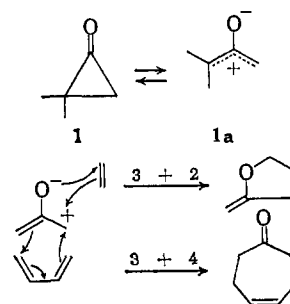
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### Cycloaddition Reactions of 2,2-Dimethylcyclopropanone<sup>1</sup>

Sir:

The application of orbital symmetry considerations has provided an important stimulus to the study of electrocyclic,<sup>2</sup> sigmatropic,<sup>3</sup> and cycloaddition<sup>4</sup> reactions. Cyclopropanones possess the unusual property of being capable of undergoing numerous cycloaddition reactions.<sup>5</sup> In order to employ the Woodward-Hoffmann rules<sup>2-4</sup> to predict the selection rules for cycloaddition reactions of cyclopropanones, it is useful to consider the reactive intermediate as a dipolar ion<sup>6</sup> (e.g., **1a**). This description indicates that two symmetry-allowed cycloadditions are possible: (a) 3 + 4 → 7 additions of cyclopropanones and dienes,<sup>5</sup> and (b) 3 + 2 → 5 additions of cyclopropanones and monoolefins.



We wish to report the first examples of 3 + 2 → 5 cycloaddition reactions of cyclopropanones.

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(3) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 2511 (1965).

(4) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 4388 (1965).

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(6) J. G. Burr, Jr., and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954).