Substitution Kinetics of Paramagnetic Iron(0) Nitrosyl Complexes. Temperature Dependence of the Arrhenius Activation Energy

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Abstract: Paramagnetic transition metal complexes of the type $Fe(NO)_2XL$, where X = Cl, Br, and I, and L = $P(C_6H_5)_3$, $P(n\text{-}C_4H_9)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$, and $As(C_6H_5)_3$, undergo halogenic substitution in the presence of phosphines to give $Fe(NO)_2L_2$ diamagnetic complexes. The rates of these reactions depend both on the halogen and on the concentration and nature of the reagent. The reactions of $Fe(NO)_2XP(C_6H_5)_3$ with $P(C_6H_5)_3$ proceed with a kinetically suitable rate and have been studied from about 253 to about 333°K. The log k_{II} *vs.* $1/T$ plots for these reactions show a distinct departure from the Arrhenius law. In each case, an increase in temperature leads to a decrease in the activation energy. Negative activation energies have been observed for the chlorine and iodine derivatives in the 293–333°K range. This is interpreted in terms of a two-step mechanism in which the postulated $Fe(NO)_2X[P(C_6H_5)_3]_2$ intermediate is partitioned between two pathways, one leading to the products and the other back to the reagents. Such partitioning is assumed to be temperature dependent.

Most of the literature kinetic data show linear log k *vs.* $1/T$ Arrhenius plots. On theoretical grounds, however, the activation energy of a given reaction is temperature dependent even for a very simple kinetic process.[1,2] Such a dependence is almost never observed for the rather limited experimental temperature range available and the limits of accuracy.

Deviations from the Arrhenius law of different nature can be found for complex reactions involving, for example equilibria[3–5] or parallel[6,7] or consecutive processes.[3–5] In those cases indeed, if a given reaction pathway becomes predominant on changing the temperature, or if different steps are rate determining over different temperature ranges, the measured activation energy will change with temperature. This, which should be a usual case, is, however, again not frequently observed for the failure of the above conditions, or for the limited accessible temperature range.

Such experimental limitation is even stronger in the case of zerovalent transition metal complexes. In these cases, indeed, poor solubility or decomposition phenomena of the substrate are the limiting factors. The present paper reports the halogen substitution kinetics of $Fe(NO)_2XPR_3$ with PR_3 (X = Cl, Br, I). It has been possible to make the study in a temperature range of about 80°. The corresponding Arrhenius plots exhibit a very distinct departure from linearity. This study represents a rather interesting case of reaction involving a paramagnetic neutral complex which gives a diamagnetic $Fe(NO)_2(PR_3)_2$ species.

Experimental Section

Compounds and Solvent. The phosphine $P(C_6H_5)_3$ was obtained from Fluka and was crystallized from ethanol. The phosphines $P(n\text{-}C_4H_9)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$, $P(OC_6H_5)_3$, and $P(OCH_3)_3$ were commercial products, distilled under nitrogen before use. The reagent $As(C_6H_5)_3$ was Fluka (Puriss) and was used without further purification.

Toluene for the kinetic runs was purified according to Vogel[8] and stored under argon.

Preparation of the Complexes. The compounds $Fe(NO)_2XL$ (X = Cl, Br) were prepared[9,10] by the reaction of $[Fe(NO)_2X]_2$ with the ligand in anhydrous oxygen-free tetrahydrofuran (THF). In particular, a reaction mixture containing equimolar amounts of $[Fe(NO)_2X]_2$ and L was allowed to stand for 5 hr at room temperature.

The $P(C_6H_5)_3$ and $As(C_6H_5)_3$ derivatives are solid and were purified by repeated crystallizations[9] from acetone. The $Fe(NO)_2BrP(n\text{-}C_4H_9)_3$ and $Fe(NO)_2BrP(O\text{-}i\text{-}C_3H_7)_3$ complexes, which had not been previously described, are red-brown oils; they were purified by column chromatography on Al_2O_3, using a 1:1 mixture of dichloromethane and hexane as eluent. Partial decomposition occurred on the column, even using oxygen-free eluent. The eluent was removed under reduced pressure at room temperature.

These last samples were identified by their mass[11] and infrared spectra. Their N–O stretching frequencies, and those of other $Fe(NO)_2XL$ and $Fe(NO)_2L_2$ complexes, are collected in Table I. Mass spectrometric and infrared analysis showed no detectable impurities in the substrates used for the kinetic runs.

The final products of the studied kinetics $Fe(NO)_2L_2$ (L = $P(C_6H_5)_3$, $P(n\text{-}C_4H_9)_3$, and $P(O\text{-}i\text{-}C_3H_7)_3$) were prepared by allowing $Fe(NO)_2BrL$ and the corresponding ligand L to stand in anhydrous oxygen-free THF at 40° for about 5 hr. The compounds were purified in a manner very similar to that used for $Fe(NO)_2BrP(n\text{-}C_4H_9)_3$.

The intermediate $[Fe(NO)_2I]_2$ necessary to prepare the complex, $Fe(NO)_2IP(C_6H_5)_3$, was obtained by absorption of NO gas on a mixture of reduced iron powder and freshly sublimed iodine. Iodine crystals were finely mixed under nitrogen with a slight excess of iron powder. The mixture was allowed to absorb, in a reactor at room temperature, NO gas from a generator. The reaction starts quickly with a strong release of heat. It was therefore neces-

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Table I. N–O Stretching Frequencies[a] for $Fe(NO)_2XL$ and $Fe(NO)_2L_2$ Complexes in CCl_4

Complex	ν_{NO}, cm^{-1}	
$Fe(NO)_2BrP(C_6H_5)_3$	1790	1734
$Fe(NO)_2ClP(C_6H_5)_3$	1789	1731
$Fe(NO)_2IP(C_6H_5)_3$	1789	1738
$Fe(NO)_2BrP(O\text{-}i\text{-}C_3H_7)_3$	1799	1739
$Fe(NO)_2BrP(n\text{-}C_4H_9)_3$	1783	1727
$Fe(NO)_2BrAs(C_6H_5)_3$	1790	1734
$Fe(NO)_2[P(C_6H_5)_3]_2$	1721	1677
$Fe(NO)_2[P(n\text{-}C_4H_9)_3]_2$	1704[b]	1661[b]
$Fe(NO)_2[P(O\text{-}i\text{-}C_3H_7)_3]_2$	1730[b]	1682[b]

[a] All spectra were calibrated with polystyrene film using the peak at 1602 cm^{-1}. [b] Toluene solution.

sary to control the reaction by cooling the reactor with an ice bath.

Kinetic Studies. Purified anhydrous toluene was used as the solvent in all the experiments. The reaction mixtures were obtained by mixing solutions of the reactants, prethermostated at the desired temperature. They were kept in ampoules at constant temperature, in the dark, and under a nitrogen atmosphere during the kinetic runs. The kinetics were carried out under pseudo-first-order conditions, using at least a tenfold excess of the entering ligand; the reactions were followed spectrophotometrically as described below, with a Perkin-Elmer Model 337 ir instrument. Measurements were usually made over a period of three half-times of the kinetics. All reactions went to completion. The data gave good linear plots of $\log (D_0 - D_\infty)/(D - D_\infty)$ *vs.* t, where t is the time, D_0 is the absorption at zero time, D is the absorption at time t, and D_∞ is the absorption at infinite time. Estimated rate constants were reproducible to within 15% or better. The values of $\Delta H^{\ddagger}$ are estimated to be accurate to ±3 kcal/mol and $\Delta S^{\ddagger}$ to ±8 eu.

The rates of reaction of $Fe(NO)_2XL$ were followed by observing changes in the N–O stretching region of the spectra to record the disappearance of starting material and/or appearance of product. The absorbances of the symmetric ν_{NO} of $Fe(NO)_2XL$ and/or of the asymmetric ν_{NO} of $Fe(NO)_2L_2$ were measured. The results obtained using the two procedures agreed in all cases.

Blank runs with the initial or final complexes showed that they were sufficiently stable even at 50°. Rate constants of the thermal decomposition processes were of the order of 10^{-7}–10^{-8} sec^{-1} at this temperature, and therefore it has been assumed that the kinetic measurements were not appreciably affected by this process.

During the kinetic runs of the reaction between $Fe(NO)_2BrP(C_6H_5)_3$, and $P(C_6H_5)_3$ a white gelatinous precipitate, partially soluble in H_2O or in organic solvents, was observed. Its amount was apparently dependent on the concentration of the starting complex. It had the physical appearance of the precipitate which is immediately formed by adding Br_2 to a solution of $P(C_6H_5)_3$ in cyclohexane. It was therefore assumed that the precipitate observed during the kinetic runs was due to the reaction of the bromine eliminated from $Fe(NO)_2BrP(C_6H_5)_3$ with the reagent $P(C_6H_5)_3$.

In order to test the influence of the bromine on the kinetics studied, different runs were made by adding to the reaction mixture in toluene small amounts of a titrated solution of bromine in cyclohexane.[12] The k_{II}'s obtained were not appreciably influenced by the bromine addition.

The above study pointed out that under the pseudo-first-order conditions used throughout the work, all the evolved halogen was caught by the phosphine, being therefore prevented from reacting with the initial or final complexes. On the other hand, the percentage of phosphine precipitation was small enough to give errors within the reported limits. Kinetic runs made by adding aliquots of the above white precipitate (obtained from independent runs) did not show any significant variation of k_{II}. Similar phenomena were observed during the other kinetic studies involving the various $Fe(NO)_2XL$ complexes.

Results

Reaction of $Fe(NO)_2XP(C_6H_5)_3$ with $P(C_6H_5)_3$. The experimental rate constants, k_{obsd}, and the estimated second-order rate constants, k_{II}, are collected in Table II for the reaction of $Fe(NO)_2BrP(C_6H_5)_3$ with $P(C_6H_5)_3$. The table gives the rate data at the various concentrations of reagent, and at different temperatures.

Table II. Rate Constants for the Reaction between $Fe(NO)_2BrP(C_8H_5)_3$ and $P(C_6H_5)_3$ in Toluene

[C], $M \times 10^2$	[L], $M \times 10$	k_{obsd}, sec^{-1}	k_{II}, M^{-1} sec^{-1}	Temp, °C
2.00	5.17	0.84×10^{-4}	1.71×10^{-4}	60
1.93	6.78	1.33×10^{-4}	1.95×10^{-4}	60
1.91	7.49	1.64×10^{-4}	2.18×10^{-4}	60
1.90	8.40	1.63×10^{-4}	1.94×10^{-4}	60
1.49	1.48	1.5×10^{-5}	1.01×10^{-4}	50
1.43	4.53	4.45×10^{-5}	0.98×10^{-4}	50
2.06	4.53	5.56×10^{-5}	1.23×10^{-4}	50
2.07	6.54	7.82×10^{-5}	1.2×10^{-4}	50
1.99	6.65	9.04×10^{-5}	1.37×10^{-4}	50
1.34	6.72	6.9×10^{-5}	1.03×10^{-4}	50
1.30	7.08	8.3×10^{-5}	1.17×10^{-4}	50
1.99	8.31	10.29×10^{-5}	1.24×10^{-4}	50
1.99	4.20	5.14×10^{-5}	1.22×10^{-4}	40
1.97	5.15	5.55×10^{-5}	1.08×10^{-4}	40
1.95	6.09	7.63×10^{-5}	1.25×10^{-4}	40
1.93	6.64	7.96×10^{-5}	1.20×10^{-4}	40
1.99	6.66	9.60×10^{-5}	1.44×10^{-4}	40
2.00	7.03	10.00×10^{-5}	1.43×10^{-4}	40
1.99	7.51	11.20×10^{-5}	1.49×10^{-4}	40
1.95	7.54	10.60×10^{-5}	1.41×10^{-4}	40
1.99	8.32	11.30×10^{-5}	1.36×10^{-4}	40
1.99	6.66	7.53×10^{-5}	1.13×10^{-4}	30
2.01	8.64	10.07×10^{-5}	1.2×10^{-4}	30
1.93	6.65	6.13×10^{-5}	9.22×10^{-5}	22
1.93	7.49	5.76×10^{-5}	7.69×10^{-5}	22
1.90	7.54	7.13×10^{-5}	9.46×10^{-5}	22
1.95	8.32	6.14×10^{-5}	7.38×10^{-5}	22
1.93	8.33	8.6×10^{-5}	10.3×10^{-5}	22
2.00	8.86	6.67×10^{-5}	7.53×10^{-5}	22
1.93	9.19	9.74×10^{-5}	10.6×10^{-5}	22
1.96	6.65	0.80×10^{-5}	1.2×10^{-5}	0
1.97	7.49	1.06×10^{-5}	1.4×10^{-5}	0
1.89	8.31	1.1×10^{-5}	1.32×10^{-5}	0
1.88	9.09	1.29×10^{-5}	1.42×10^{-5}	0
1.78	9.11	1.19×10^{-5}	1.3×10^{-5}	0
1.91	6.67	1.71×10^{-6}	2.57×10^{-6}	−18
1.94	7.57	1.86×10^{-6}	2.46×10^{-6}	−18
1.89	8.38	2.42×10^{-6}	2.89×10^{-6}	−18
1.93	9.13	2.31×10^{-6}	2.53×10^{-6}	−18

Table III. Rate Constants for the Reaction between $Fe(NO)_2ClP(C_6H_5)_3$ and $P(C_6H_5)_3$ in Toluene

[C], $M \times 10^2$	[L], $M \times 10$	k_{obsd}, sec^{-1}	k_{II}, M^{-1} sec^{-1}	Temp, °C
2.00	3.22	1.87×10^{-5}	5.81×10^{-5}	60
1.99	4.20	2.50×10^{-5}	5.95×10^{-5}	60
2.01	4.91	2.68×10^{-5}	5.47×10^{-5}	60
2.01	6.65	4.04×10^{-5}	6.08×10^{-5}	60
2.02	8.34	4.04×10^{-5}	5.98×10^{-5}	60
2.04	4.50	2.31×10^{-5}	5.13×10^{-5}	50
2.02	5.46	2.86×10^{-5}	5.24×10^{-5}	50
2.00	6.66	3.45×10^{-5}	5.20×10^{-5}	50
2.01	7.50	3.59×10^{-5}	4.79×10^{-5}	50
2.11	8.35	3.96×10^{-5}	4.74×10^{-5}	50
2.01	5.50	5.8×10^{-5}	1.06×10^{-4}	30.4
1.98	7.62	7.02×10^{-5}	0.92×10^{-4}	30.4
2.15	5.92	0.71×10^{-4}	1.2×10^{-4}	21.4
2.13	7.77	0.78×10^{-4}	0.98×10^{-4}	21.4
2.08	7.64	1.02×10^{-4}	1.34×10^{-4}	20.6
2.07	8.47	1.15×10^{-4}	1.36×10^{-4}	20.6
2.12	7.63	5.04×10^{-4}	0.66×10^{-4}	0
2.17	6.67	0.82×10^{-5}	1.22×10^{-5}	−14
2.13	7.51	0.83×10^{-5}	1.10×10^{-5}	−14
2.11	8.39	1.09×10^{-5}	1.3×10^{-5}	−14

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[12] Cyclohexane was used as solvent for the stock bromine solution, since the halogen reacts with toluene. This fact made it difficult to prepare titrated solutions of bromine in toluene.

Table IV. Rate Constants for the Reaction between $Fe(NO)_2IP(C_6H_5)_3$ and $P(C_6H_5)_3$ in Toluene

[C], $M \times 10^2$	[L], $M \times 10$	k_{obsd}, sec^{-1}	k_{I1}, $M^{-1}\ \mathrm{sec}^{-1}$	Temp, °C
1.75	1.87	6.65×10^{-5}	3.55×10^{-4}	60
1.74	3.59	1.10×10^{-4}	3.07×10^{-4}	60
1.76	5.61	7.85×10^{-4}	1.40×10^{-3}	45
1.76	5.77	8.24×10^{-4}	1.43×10^{-3}	20
1.73	7.56	1.20×10^{-3}	1.58×10^{-3}	20
1.75	6.66	3.27×10^{-4}	4.90×10^{-4}	0
1.71	7.55	7.17×10^{-5}	0.95×10^{-4}	−19

Rate data for the corresponding reactions involving $Fe(NO)_2ClP(C_6H_5)_3$ and $Fe(NO)_2IP(C_6H_5)_3$ are given in Tables III and IV, respectively.

Reaction of $Fe(NO)_2BrL$ with L (L = $P(O\text{-}i\text{-}C_3H_7)_3$, $P(n\text{-}C_4H_9)_3$). These kinetic studies, made under conditions similar to those used for the other reactions, were very fast at 20°. During the time necessary for the mixing of the reactants (previously thermostated) and for sampling in the infrared cell (about 0.5 min) the reactions went to about 70–80% completion, giving the $Fe(NO)_2L_2$ products.

Reaction of $Fe(NO)_2BrM(C_6H_5)_3$ with $As(C_6H_5)_3$ (M = As, P). These reactions, in experimental conditions similar to those adopted for the other kinetics studied here, did not occur.[13] The $Fe(NO)_2BrAs(C_6H_5)_3$ complex decomposed with $k_{\mathrm{obsd}} = 10^{-7}–10^{-8}$ sec^{-1} at 50°. The reaction was followed for 1 week.

Reaction of $Fe(NO)_2BrAs(C_6H_5)_3$ with $P(C_6H_5)_3$. The rate data for this reaction at 50° are reported in Table V. The close similarity of the k_{II} for this reaction and for the corresponding reaction of $Fe(NO)_2BrP(C_6H_5)_3$ with $P(C_6H_5)_3$ is remarkable.

Table V. Rate Constants for the Reaction between $Fe(NO)_2BrAs(C_6H_5)_3$ and $P(C_6H_5)_3$ in Toluene at 50°

[C], $M \times 10^2$	[L], $M \times 10$	k_{obsd}, sec^{-1}	k_{II}, $M^{-1}\ \mathrm{sec}^{-1}$
2.06	4.53	5.56×10^{-5}	1.23×10^{-4}
2.07	6.54	7.82×10^{-4}	1.20×10^{-4}
2.11	8.36	1.02×10^{-5}	1.22×10^{-4}

Reaction of $Fe(NO)_2BrP(C_6H_5)_3$ with $P(OC_6H_5)_3$. The reaction occurred with a rate apparently of the same order of magnitude as that of the reaction between $Fe(NO)_2BrP(C_6H_5)_3$ and $P(C_6H_5)_3$. The overlap of the infrared bands of the initial and final complexes prevented, however, obtaining quantitative kinetic data.

Reaction of $Fe(NO)_2BrP(C_6H_5)_3$ with $P(OCH_3)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$, or $P(n\text{-}C_4H_9)_3$. The reactions were very fast. They went to about 80–90% completion almost instantaneously. In the above last three types of reactions, we have been unable to discriminate between the two possible kinds of final products, ($Fe(NO)_2L_2$ or $Fe(NO)_2LL'$).[14] These complexes should have indeed rather close N–O stretching frequency values, and no attempt was made to analyze the final products with other analytical tools.

Discussion

The kinetic data reported in Tables II, III, IV, and V give evidence for the second-order nature of the halogen substitution reaction in the temperature range studied. The reaction is first order in the concentrations of both the substrate and the reagent.

The SN2 mechanism is confirmed by the linearity of the k_{obsd} *vs.* [L] plots. The zero intercept of these plots suggests that no appreciable SN1 contribution is present, as frequently found[16,17] instead in kinetics involving organometallic complexes.

The reaction studied clearly depends on the nature of the halogen and in a stronger way on the nature of the entering ligand, L.

In the low-temperature range (around 0°) the reaction rates are in the order I (50) > Cl (6) > Br (1), while at higher temperatures (around 50°) the situation becomes I (25) > Br (2) > Cl (1). In both cases, therefore, the iodine causes a rather large increase of the reaction rate, as frequently found in kinetics involving organometallic complexes.[17,18]

The influence of the entering ligand, L, on the reaction rate may be explained at least in part in terms of its donor ability. In particular, the reactions involving the ligands $P(n\text{-}C_4H_9)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$, and $P(OCH_3)_3$ occur almost instantaneously either on a substrate containing a PR_3 ligand equal to the entering one, or on the substrate containing $P(C_6H_5)_3$. On the other hand, in the experimental conditions adopted here, the reactions involving a poor nucleophile like $As(C_6H_5)_3$ do not occur both on $Fe(NO)_2BrP(C_6H_5)_3$ and on $Fe(NO)_2BrAs(C_6H_5)_3$. Ligands having intermediate donor abilities, like $P(C_6H_5)_3$ and $P(OC_6H_5)_3$, react with intermediate finite rates.[19]

In addition, when the $P(C_6H_5)_3$ ligand reacts with $Fe(NO)_2BrAs(C_6H_5)_3$ and $Fe(NO)_2BrP(C_6H_5)_3$, very similar reaction rates are observed. This is in agreement with the fact that the main role in determining the rate of reaction is played here by the nature of the entering ligand. In fact, it is to be noted that the magnitude of the effects caused by the entering ligands is unusually large when compared to the same effects in substitution kinetics involving other organometallic complexes.[17,18] This magnification effect might be connected to the particular nature of the paramagnetic substrates studied here.

In any case, the above discussion confirms that a second-order mechanism is effective in these reactions.

A better insight into the reaction mechanism is given by the study of the activation parameters. Among the reactions studied, it has been possible to obtain the values of these functions for the reactions between $Fe(NO)_2XP(C_6H_5)_3$ and $P(C_6H_5)_3$ only. No attempt was made to determine these parameters for other reactions, since they were too fast or the final products were unidentified.

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(13) W. Hieber and R. Kramolowsky, *Z. Anorg. Allg. Chem.*, 321, 94 (1963).

(14) These products were hypothesized by analogy with the reaction[15] involving $Co(CO)_2NOP(C_6H_5)_3$, where $P(OC_6H_5)_3$ can displace $P(C_6H_5)_3$.

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(19) In fact, the basicities of $P(OCH_3)_3$ and $P(O\text{-}i\text{-}C_3H_7)_3$ do not greatly differ[20] from that of $P(C_6H_5)_3$, so that the behavior of the phosphites suggests that entropic and/or steric hindrance factors could also play an important role in determining the rate of the reactions studied.

(20) As estimated by E. M. Thorsteinson and F. Basolo, *J. Amer. Chem. Soc.*, 88, 3929 (1966).

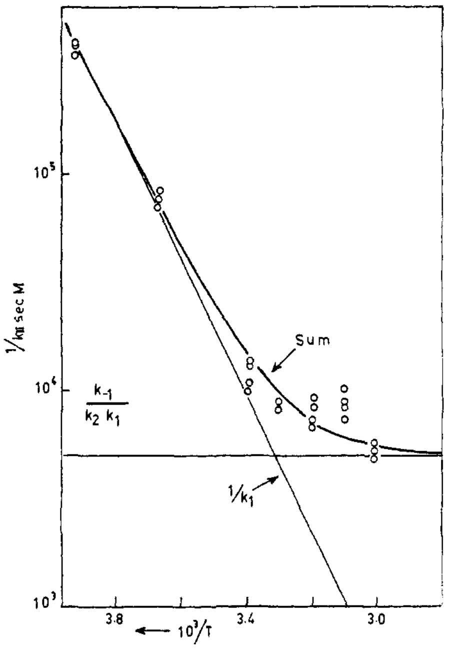

Figure 1. Arrhenius plot for the reaction $Fe(NO)_2BrP(C_6H_5)_3 + P(C_6H_5)_3 \rightarrow Fe(NO)_2[PC_6H_5)_3]_2 + Br$.

The plots of log k_{II} *vs.* $1/T$ clearly show a distinct deviation from linearity; the apparent activation energies decrease so markedly with the temperature that in the high-temperature range negative values can be obtained.

Such peculiarity of the Arrhenius plots has not been previously reported, as far as we know, for reactions involving organometallic complexes.[17,18] It can be interpreted in different ways, all corresponding to previously reported cases[3–7,21–25] for other kinds of systems.

First of all, it should be noted that the variation of the activation energy with the temperature is in the opposite direction to that which would take place if it were caused by the incursion of a parallel pathway.[5] This rules out this cause as an explanation of the present finding.

Another likely cause of curvature in the Arrhenius plots is the intervention at lower temperatures of a heterogeneous reaction. Since such reactions often have a low frequency factor and a low activation energy, they may predominate at the lower end of the temperature range.[25] Also this cause implicates, therefore, when operative, an increase of the activation energy with temperature, so that it cannot explain the present results.

The formation of an inhibitor (*e.g.*, from slight decomposition of some partner of the reacting system) in the high-temperature range might in principle explain the failure of the Arrhenius law now observed. Also some kind of homogeneous catalysis should act in the same direction, if the catalyst were decomposed on increasing the temperature. The last two possibilities seem, however, to be ruled out in the present cases, since a kinetic run on the bromine derivative started at 50° and then cooled to 0° gave a k_{II} value close to that obtained for the corresponding kinetics for the reaction run completely at 0°.

In these conditions, by assuming[26] that the ΔC_p of the present reactions is not too large, the only possibility to explain the observed failure of the Arrhenius law is to invoke the occurrence of a reaction sequence involving some kind of equilibrium. In this respect, at least two reaction sequences can be hypothesized.[27]

In particular, one can hypothesize a reaction sequence in which the final product should be formed at low temperature, from a dimeric $[Fe(NO)_2XP(C_6H_5)_3]_2$ species for reaction with the entering ligand, while at temperatures higher than 20° the dimer would be almost entirely dissociated in monomeric species which would react with the entering ligand. Such a mechanism does not seem satisfactory, however, since kinetic runs made with different concentrations of the complex gave coincident results.

By contrast, a satisfactory scheme which explains the present results is the following.

$$\begin{tikzcd}
Fe(NO)_2XP(C_6H_5)_3 + P(C_6H_5)_3 \arrow[r, shift left, "k_1"] & Fe(NO)_2X[P(C_6H_5)_3]_2 \arrow[l, shift left, "k_{-1}"] \arrow[d, "k_2"] \\
& Fe(NO)_2[P(C_6H_5)_3]_2 + X \quad (1)
\end{tikzcd}$$

It represents a simplified version of the usually postulated associative substitution reaction path.[16,18] By assuming the steady-state approximation, the reaction rate is given by

$$v = \frac{-d[Fe(NO)_2XP(C_6H_5)_3]}{dt} = \frac{d[Fe(NO)_2[P(C_6H_5)_3]_2}{dt} = \frac{k_1k_2}{k_{-1} + k_2}[Fe(NO)_2XP(C_6H_5)_3][P(C_6H_5)_3] = k_{II}[\text{substrate}][\text{ligand}] \quad (2)$$

This equation describes well the observed curvature in the Arrhenius plots and also the negative values of the activation energies in the high-temperature range, when it is assumed that k_{-1} increases with the temperature much faster than k_2.

If one writes the above equation in its reciprocal form,[28] it is seen that the reciprocal of k_{II}

$$\frac{1}{k_{II}} = \frac{1}{k_1} + \frac{k_{-1}}{k_2k_1}$$

plotted in the Arrhenius way (see Figures 1–3), must be the arithmetic sum of two Arrhenius straight lines, which asymptotically approach the curve and can be constructed by an easy iterative calculation. The low-temperature limiting line corresponds to a situation in which k_2 is much larger than k_{-1} and k_1 is the rate constant of the slow step of the reaction, so that the

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(21) V. R. Gurevich, M. A. Dalin, and K. M. Arntyunove, *Azerb. Khim. Zh.*, 69, (1964).

(22) E. S. Rudakov and Ya. Kivalin (*Reakt. Sposobnost. Org. Soedin.*), *Chem. Abstr.*, 62, 7600*c* (1965).

(23) A. W. Murray, *Biochim. J.*, 103, 271 (1967).

(24) R. E. Robertson, *Solvation Phenomena, Symp. Repr.*, 1, 20 (1963); *Chem. Abstr.*, 64, 11937*d* (1966).

(25) A. Maccoll in ref 4, Part I, p 454.

(26) For the limits of validity of this assumption, see ref 2.

(27) The intervention of an equilibrium between a neutral species $Fe(NO)_2XP(C_6H_5)_3$ and the ions $Fe(NO)_2P(C_6H_5)_3^+$ and X^- is to be ruled out because of the low polarity of the solvent used.

(28) We are very much obliged to a referee for having suggested this kind of representation of the data.

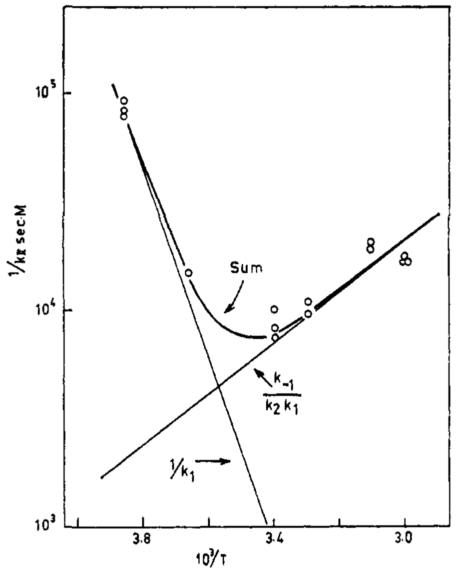

Figure 2. Arrhenius plot for the reaction $Fe(NO)_2IP(C_6H_5)_3 + P(C_6H_5)_3 \rightarrow Fe(NO)_2[P(C_6H_5)_3]_2 + I$.

rate expression becomes

$$v = k_1[\text{substrate}][\text{ligand}] \quad (3)$$

The high-temperature limiting line corresponds instead to a situation in which k_{-1} is large compared to k_2, so that a preequilibrium occurs, followed by a rate-determining step, and the rate expression becomes

$$v = k_2K_{eq}[\text{substrate}][\text{ligand}] \quad (4)$$

This equation leads to a negative slope of the Arrhenius plot when K_{eq} decreases by increasing the temperature and the normal increase in k_2 is of smaller magnitude.

The rate constant expression (2) cannot be simplified in the intermediate temperature region, since k_{-1} and k_2 are then approximately of the same order of magnitude.

In these conditions the activation parameters which can be obtained from the low-temperature limiting line correspond to the associative step of the proposed mechanism, while those from the high-temperature limiting line correspond to the sum of the activation parameters of the preequilibrium and of step 2. These activation parameters are reported in Table VI; it is immediately seen that those for the low-temperature range are consistent[17, 18] with the above provision.

Conclusions

The reactions discussed here represent a rather interesting case in which two different situations prevail as a function of temperature and can be easily detected experimentally. That which should be a frequently observed case is often not observed, sometimes only for the limited accessible temperature range. The present examples point out the general opportunity to estimate the thermal parameters over a range of temperatures as large as possible.

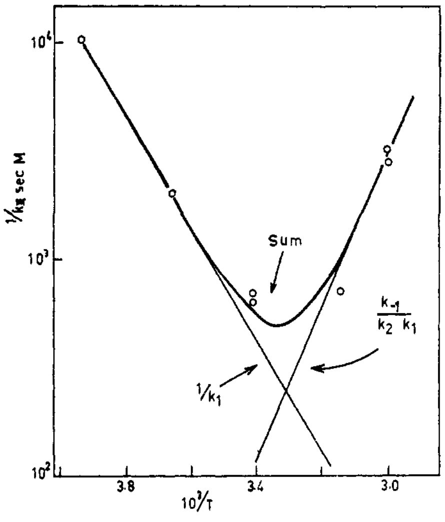

Figure 3. Arrhenius plot for the reaction $Fe(NO)_2ClP(C_6H_5)_3 + P(C_6H_5)_3 \rightarrow Fe(NO)_2[P(C_6H_5)_3]_2 + Cl$.

Any kinetics involving a complex reaction sequence should show indeed, when examined in a suitable range of temperature, a distinct curvature in the Arrhenius plot, and its interpretation is most important in assessing a given reaction mechanism. This holds only if the energies of activation of the various alternate pathways, among which the intermediate or the reactants themselves can be partitioned, are sufficiently different. In this case, of course, the proportion of the total reaction going by one pathway or the other will vary with temperature.

Table VI. Activation Parameters for the Reaction between $Fe(NO)_2XP(C_6H_5)_3$ and $P(C_6H_5)_3$ in Toluene

	Low-temperature limit		High-temperature limit
	$\Delta H_1^{\ddagger}$, kcal mol^{-1}	$\Delta S_1^{\ddagger}$ ($-10°$), eu	$\Delta H_2^{\ddagger} + \Delta H_1°$, kcal mol^{-1}
Cl	20.0	−6	−5.4
Br	14.5	−29	0
I	11.4	−34	−16

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