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Mechanisms of Elimination Reactions. 33. Carbon Isotope Effects in E2 Reactions of (2-Phenylethyl-*2*-^{14}C)trimethylammonium Ion. The Role of Tunneling[1]

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Abstract: Carbon isotope effects have been determined for the reactions of (2-phenylethyl-*2*-^{14}C)trimethylammonium ion with hydroxide ion in 10, 25, 40, and 60% Me_2SO–water and with ethoxide ion in dry ethanol. Comparison of these values with earlier results on ^{13}C isotope effects shows that the relation between the ^{14}C and ^{13}C effects is close to that predicted from theory. The magnitudes of the isotope effects suggest significant contributions from tunneling, and this suggestion is supported by temperature-dependence studies that give ΔE_a values too large and $A_{a(12)}/A_{a(14)}$ values too small to account for without tunneling. Temperature dependences calculated from the Bell theory of tunneling can be fitted to the experimental data. The results indicate that the semiclassical (without tunneling) carbon isotope effects are small or even inverse and that tunnel corrections make major contributions to the observed isotope effects.

Some time ago we studied β-^{13}C isotope effects in the E2 reactions of (2-phenylethyl)dimethylsulfonium and (2-phenylethyl)trimethylammonium ions with hydroxide ion in mixtures of dimethyl sulfoxide and water.[3,4] Each of these substrates shows a maximum in k_H/k_D (for the β-2,2-d_2 species)[5-7] as a function of dimethyl sulfoxide concentration, a circumstance under which the proton is expected to be half-transferred in the transition state.[8,9] Model calculations predict that $(k_{12/13})_s$, which represents the semiclassical (without tunneling) contribution to the isotope effect, should at approximately half-transfer of the proton be somewhat below unity (an *inverse* effect) or at best only slightly above unity. A contribution from tunneling was predicted, however, to lead to an overall isotope effect in the normal direction ($k_{12}/k_{13} > 1$).[4,10,11] The observed k_{12}/k_{13} values were in the range 1.015–1.030, and comparison with the model calculations suggested that the tunnel correction was a substantial part of the observed effect, at least 1.015–1.020.

The role of tunneling in deuterium and tritium isotope effects is not entirely free of controversy, and the idea that tunneling can contribute to heavy-atom isotope effects may seem particularly strange to some. In the light of theory the idea is entirely respectable. It should be kept in mind that the reacting system as a whole tunnels, not a particular atom. Thus the common practice of speaking of hydrogen tunneling in chemical reactions is not really correct. Attention has been focused almost entirely on hydrogen transfers because they are expected to show a low effective mass along the reaction coordinate and hence a reaction coordinate frequency, $\nu^{\ddagger}{}_L$, of large absolute magnitude. If the reaction coordinate consists almost entirely of proton motion, the effective mass along the reaction coordinate, $m^{\ddagger}$, will be close to the mass of hydrogen. In that case, $m^{\ddagger}$ will be essentially doubled by the substitution of deuterium for protium, but very little influenced by substitution of ^{13}C or ^{14}C for ^{12}C in the donor atom. If, on the other hand, heavy-atom motion contributes significantly to the reaction coordinate, $m^{\ddagger}$ will be larger, less sensitive to changes in hydrogen mass, and more sensitive to changes in carbon mass.[14] Thus the sensitivity of $\nu^{\ddagger}_L$ to isotopic substitution in the donor atom can be small for pure proton transfers, but quite significant when the proton transfer is coupled with heavy-atom motion in the reaction coordinate. The magnitude of a moderate-size tunnel correction is determined by the absolute magnitude and isotopic sensitivity of $\nu^{\ddagger}_L$, for eq 1 describes the tunnel correction

$$Q_t = (u_t/2)/\sin (u_t/2) \qquad (1)$$

$$u_t = h|\nu^{\ddagger}{}_L|/kT \qquad (2)$$

as well as any one-dimensional treatment when $u_t < 2\pi$ and the barrier height is substantial.[12,13] It is very probable that our reactions fall within these limitations.[7]

In spite of these arguments for the reasonableness of tunneling contributions to carbon isotope effects, we recognize that the experimental evidence for the idea must be strong to achieve general acceptance. We have recently published additional evidence in a different system, proton abstraction from 2-nitropropane-*2*-^{14}C by pyridine bases,[14] and the present study was intended to provide critical tests of the evidence in the case of the E2 reaction.

With few exceptions, heavy-atom isotope effects are too small to determine precisely by direct rate measurement, and competitive methods requiring the measurement of small changes in isotopic composition of the reactant or product of a chemical reaction must be used. In the case of carbon, one of the two important heavy isotopes (^{13}C) is stable and measurable by mass spectrometry, and the other (^{14}C) is unstable and measurable by radioactivity determination. Fortunately, the major sources of error in these two approaches to determination of carbon isotope effects are quite different.[15] In addition, the relationship between ^{13}C and ^{14}C isotope effects can be shown to be given rather accurately by eq

$$[\ln (k_{12}/k_{14})]/[\ln (k_{12}/k_{13})] = r \qquad (3)$$

3 with $r \approx 1.9$.[16-18] If ^{14}C and ^{13}C isotope effects determined

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Table I. ^{14}C and ^{13}C Isotope Effects for the Reactions of (2-Phenylethyl)trimethylammonium Ion with Hydroxide Ion in Mixtures of Water and Dimethyl Sulfoxide and with Ethoxide Ion in Ethanol

Me_2SO, %[a]	T, °C[b]	k_{12}/k_{14}[c]	k_{12}/k_{13}[c,d]	r[e]
10	40	1.0440 ± 0.0014		
10	60	1.0348 ± 0.0009	1.0161 ± 0.0004	2.14
10	80	1.0281 ± 0.0008	1.0146 ± 0.0003	1.91
25	60	1.0309 ± 0.0052		
40	40	1.0458 ± 0.0009		
40	60	1.0318 ± 0.0008	1.0161 ± 0.0014	1.96
40	80	1.0301 ± 0.0009	1.0169 ± 0.0013	1.77
60	40	1.0430 ± 0.0023		
60	60	1.0338 ± 0.0016	1.0210 ± 0.0015	1.60
60	80	1.0222 ± 0.0089		
f	40	1.0448 ± 0.0002		
f	50	1.0387 ± 0.0010		
f	60	1.0313 ± 0.0007		
f	70	1.0277 ± 0.0007		

[a] Mole percent. [b] ±0.05 °C. [c] Deviation is standard deviation of the mean. [d] From ref 4. [e] $\ln (k_{12}/k_{14})/\ln (k_{12}/k_{13})$. [f] In dry ethanol with ethoxide ion as base.

under identical conditions conform to this relation, they are almost certainly both correct, for it is highly unlikely that both would suffer from systematic error of the same direction and magnitude.

The isotope effects were obtained by allowing (2-phenylethyl-*2*-^{14}C)trimethylammonium ion to react with base to a measured fraction of reaction, F, and comparing the activity (R) of recovered substrate with that (R_0) of the original substrate, using eq 4[19] to calculate k_{12}/k_{14}.

$$\frac{k_{12}}{k_{14}} = \frac{\log (1 - F)}{\log [(1 - F)R/R_0]} \tag{4}$$

The fraction of reaction was at first varied widely to guard against systematic error. No trends of k_{12}/k_{14} with F were observed; so most runs were done in a range of F (0.6–0.8) that gives the least effect of error in F and R/R_0 on k_{12}/k_{14}. The ammonium salt was in all cases oxidized to benzoic acid, which was easier than the salt itself to isolate in a pure state for activity measurement. The oxidation had been shown to be nearly quantitative and to give benzoic acid of constant isotopic composition from a given sample of ammonium salt.[4] A check on the benzoic acid from oxidation of the radioactive substrate in both water and water–Me_2SO confirmed our experience in the ^{13}C work. Further details of the measurements and the synthesis of the labeled substrate are given in the Experimental Section.

The results are collected in Table I and compared with ^{13}C isotope effects from our earlier work.[4] The uncertainties are comparable in the two sets of data, especially when account is taken of the greater magnitude of the ^{14}C effects. The ratio r (eq 3) is close to the theoretical value of 1.9 in nearly all cases. The average of all the values of r is 1.88, suggesting that the observed deviations from 1.9 in individual cases are simply the result of random error. Even the worst deviation, at 60 °C in 60% Me_2SO, is hardly major; the value of k_{12}/k_{13} predicted from k_{12}/k_{14} and $r = 1.9$ is 1.0176, compared to the observed 1.0210. The question of whether $r \approx 1.9$ still applies when tunnel corrections to the carbon isotope effect as large as those claimed below are present was settled by model calculations similar to those we have previously reported on the E2 reaction of ethyl chloride with hydroxide ion.[10] While r is slightly lower for the overall than for the semiclassical isotope effects, the difference is trivial; all values of r were in the range 1.86–1.92, and the greatest difference (for an 8% tunnel effect) was 0.05. We feel justified in claiming a very strong presumption that both k_{12}/k_{13} and k_{12}/k_{14} values are essentially correct. The experimental basis of our conclusion that the carbon isotope effects contain important contributions from tunneling is thus strengthened.

Table II. Arrhenius Parameters of the ^{14}C Isotope Effects for the Reactions of (2-Phenylethyl)trimethylammonium Ion with Hydroxide Ion in Mixtures of Water and Dimethyl Sulfoxide and with Ethoxide Ion in Ethanol

Me_2SO, %[a]	$E_{a(14)} - E_{a(12)}$,[b] cal mol^{-1}	$A_{a(12)}/A_{a(14)}$[b]
10	84.4 ± 7.6	0.911 ± 0.011
40	84.3 ± 14.4	0.912 ± 0.020
60	110.5 ± 35.6	0.873 ± 0.047
c	120.8 ± 11.5	0.860 ± 0.015

[a] Mole percent. [b] Deviations are standard deviations from a linear least-squares fit. Each experimental value was used separately, not the averages at each temperature quoted in Table I. See footnote 20 for meaning of notation. [c] In dry ethanol with ethoxide ion as base.

The other aspect of our evidence for tunneling was the temperature dependence of k_{12}/k_{13}. The semiclassical isotope effects were predicted from calculations on models with the proton approximately half-transferred to show an inverse temperature dependence (k_{12}/k_{13} increasing with increasing temperature), but in two of three cases examined, k_{12}/k_{13} decreased significantly with increasing temperature, the behavior expected from tunneling.[4,11] Only two temperatures 20° apart were studied, however, precluding meaningful determination of Arrhenius parameters. To provide more reliable evidence on the temperature dependence of k_{12}/k_{14}, we covered a 40 °C (30 °C in the case of ethoxide in ethanol) range. The results, expressed as Arrhenius parameters from a linear least-squares fit, are given in Table II.

It is evident that the temperature dependence is rather steeply normal in all cases and that $A_{a(12)}/A_{a(14)}$[20] is well below unity. This latter fact is particularly diagnostic, for model calculations give ratios of Arrhenius preexponential factors for ^{12}C and ^{13}C close to unity in the absence of tunneling but distinctly below unity when tunneling is included.[11] Later calculations of $(k_{12}/k_{14})_s$ on a wider range of models give A_{12}/A_{14}[20] values of 0.993–1.026,[21] still well above those in Table II. Inclusion in the calculations of tunnel corrections that give A_{aH}/A_{aD}[20] values near those observed with (2-phenylethyl-*2,2-d*$_2$)trimethylammonium ion[7] also give $A_{a(12)}/A_{a(14)}$ values around 0.9.

Although these arguments leave little doubt that tunneling contributes to our carbon isotope effects, it would be desirable to have an estimate of the magnitude of the tunnel correction. In principle it should be possible to arrive at an estimate by fitting a temperature dependence calculated from the Bell theory of tunneling to the observed temperature dependence, just as has been done previously with k_H/k_D values.[7,22] Such a fit could be made by utilizing eq 1, 2, and 5 along with eq 10 and 11 of ref 7.

$$\frac{k_{12}}{k_{14}} = \frac{A_{12}}{A_{14}} \frac{Q_{t(12)}}{Q_{t(14)}} \exp[(E_{14} - E_{12})/RT] \tag{5}$$

To arrive at values of $\nu^{\ddagger}_{L(12)}$, $\nu^{\ddagger}_{L(14)}$, and $E_{14} - E_{12}$[20] that correctly predict the observed temperature dependence, however, it is necessary to make assumptions concerning the magnitude of A_{12}/A_{14} and $\nu^{\ddagger}_{L(12)}/\nu^{\ddagger}_{L(14)}$. A reasonable range for the former of 0.99–1.03 can be estimated from the model calculations mentioned above.[21] The same model calculations give 1.006–1.030 for the latter. Rather than assign arbitrary values to both of these ratios, we chose to take $\nu^{\ddagger}_{L(12)} \equiv \nu^{\ddagger}_{LH}$ (the light species for both deuterium and carbon isotope effects is obviously the same) from the fits based on deuterium isotope effects[7] and use $\nu^{\ddagger}_{L(12)}/\nu^{\ddagger}_{L(14)}$ as an

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Table III. Tunnel Corrections in the Reaction of (2-Phenylethyl-2-^{14}C)trimethylammonium Ion with Hydroxide Ion in 40% Dimethyl Sulfoxide at 50 °C[a]

A_{12}/A_{14} [b]	$m_{H(eff)}$ [c]	$Q_{t(12)}/Q_{t(14)}$	$(k_{12}/k_{14})_s$ [d]	$\nu^{\ddagger}_{L(12)}/\nu^{\ddagger}_{L(14)}$ [e]
0.99	2.5	1.031	1.009	1.008
0.99	1.0	1.038	1.002	1.013
1.00	1.0	1.044	0.995	1.015
1.00	2.5	1.035	1.006	1.009
1.02	1.0	1.052	0.989	1.018
1.02	2.5	1.043	0.999	1.011
1.03	1.0	1.058	0.982	1.020

[a] From fits of a temperature dependence calculated from the Bell theory of tunneling to the observed temperature dependence of k_{12}/k_{14}. See text. [b] Assumed value. See footnote 20 for meaning of notation. [c] Assumed value. [d] $(k_{12}/k_{14})_s = (k_{12}/k_{14})/(Q_{t(12)}/Q_{t(14)})$, where k_{12}/k_{14} is the overall isotope effect from the fitting process, which is within ±0.2% of k_{12}/k_{14} from the Arrhenius parameters in Table II. [e] Value giving the best fit starting with $\nu^{\ddagger}_{LH}$ from a fit using the Bell theory to the temperature dependence of k_H/k_D.

Table IV. Tunnel Corrections in the Reaction of (2-Phenylethyl-2-^{14}*C*)trimethylammonium Ion with Ethoxide Ion in Ethanol at 50 °C[a]

A_{12}/A_{14} [b]	$m_{H(eff)}$ [c]	$Q_{t(12)}/Q_{t(14)}$	$(k_{12}/k_{14})_s$ [d]	$\nu^{\ddagger}_{L(12)}/\nu^{\ddagger}_{L(14)}$ [e]
0.99	4.0	1.081	0.962	1.039
0.99	5.0	1.077	0.964	1.033
0.99	6.0	1.072	0.970	1.028
1.00	6.0	1.077	0.967	1.030
1.02	6.0	1.089	0.953	1.035
1.03	6.0	1.094	0.950	1.037

[a-e] See footnotes *a-e* of Table III.

adjustable parameter. We can then carry out fits for various values of A_{12}/A_{14} within the range suggested by the model calculations. Because $\nu^{\ddagger}_{L(12)}/\nu^{\ddagger}_{L(14)}$ depends on the effective mass along the reaction coordinate, we used $\nu^{\ddagger}_{LH}$ values from fits employing various assumed values of m_H(eff) (where m_D(eff) = m_H(eff) + 1).[7] We thus obtain a range of $Q_{t(12)}/Q_{t(14)}$ values rather than a unique value, but the results are nonetheless instructive.

A selection of the fits for the reaction of (2-phenylethyl-*i*-^{14}*C*)trimethylammonium ion with hydroxide ion in 40% dimethyl sulfoxide are recorded in Table III. The extreme values are given in the first and last lines. The results corroborate the prediction from model calculations that the semiclassical isotope effect should be small or even inverse when the proton is half-transferred in the transition state (recall that k_H/k_D is at a maximum in 40% dimethyl sulfoxide) and that the tunnel correction should account for most or all of the observed normal carbon isotope effect. The values of $\nu^{\ddagger}_{L(12)}/\nu^{\ddagger}_{L(14)}$ are within the range predicted by the model calculations.

Because the temperature dependence of k_H/k_D has not been studied in 10 and 60% dimethyl sulfoxide, we cannot apply the same fitting technique. Judging from the similarity of Arrhenius parameters in these media to those in 40% dimethyl sulfoxide, however, the results would probably not be too different. The experimental data on the reaction with ethoxide in ethanol present an interesting problem, for the tunnel correction to k_H/k_D is considerably smaller than those in Me_2SO–water mixtures, but the tunnel correction to k_{12}/k_{14} appears to be at least as large in ethanol as in Me_2SO–water, judging from the Arrhenius parameters.

The results of some trial fits for the data in ethanol are recorded in Table IV. In this case it was possible to keep $\nu^{\ddagger}_{L(12)}/\nu^{\ddagger}_{L(14)}$ below or even reasonably close to the upper limit from the calculations (1.03) only when $m_{H(eff)} \geq 4.0$, corresponding to $\nu^{\ddagger}_{LH}/\nu^{\ddagger}_{LD} \leq 1.12$. Although low $\nu^{\ddagger}_{LH}/\nu^{\ddagger}_{LD}$ values are easily achieved by models with an unsymmetrically located proton in the transition state, the inverse semiclassical carbon isotope effect seems to require that any degree of unsymmetry be rather modest. It thus appears easiest to reconcile theory and experiment by assuming $m_{H(eff)}$ is large because of coupling of proton motion with heavy-atom motion and/or solvation of the proton in a relatively symmetrical transition state.

We suggested some time ago, on the basis of a small deuterium isotope effect and a large positive Hammett ρ value, that the proton was well beyond half-transferred in the transition state for reaction of (2-arylethyl)trimethylammonium ions with ethoxide ion in ethanol.[23] We pointed out recently that the low k_H/k_D could no longer be regarded as strong evidence for an unsymmetrically located proton in the transition state, for $(k_H/k_D)_s$ was in the same range as found with hydroxide ion in 30 and 50% dimethyl sulfoxide.[7] In these latter two cases, it is unlikely that the proton is very far from half-transferred. The inverse carbon isotope effect provides further evidence that we had overstated the unsymmetry of the transition state. If so, the large ρ value must indicate simply that C–N cleavage lags well behind proton transfer in the transition state, but not that the extent of proton transfer is large.

Experimental Section

Materials. Distilled water was redistilled from potassium permanganate into a clean, dry receiver and used immediately. Fisher ACS dimethyl sulfoxide was refluxed over calcium hydride and distilled under reduced pressure to give material of mp 18–18.5 °C (lit.[24] mp 18.5 °C). Mixtures of dimethyl sulfoxide and water were prepared gravimetrically. Percentages refer to mole percent. Ethanol (99%) was refluxed over magnesium for 24 h and distilled, the first 10% being discarded. Water content was determined by the method of Vogel[25] and only material containing less than 0.1% used. Sodium ethoxide solutions were prepared from sodium metal cleaned under hexane and rinsed in hexane and ethanol.

Phenylacetonitrile-α-^{14}*C*. Benzyl-α-^{14}*C* alcohol was obtained by reducing benzoic-*carboxyl*-^{14}*C* acid with lithium aluminum hydride.[26] It was converted to benzyl-α-^{14}*C* bromide by stirring and heating with 48% hydrobromic acid. The mixture was extracted with ether, and the extracts were washed with water and sodium bicarbonate and dried over potassium carbonate. The dried extract was concentrated on a rotary evaporator. The residue was taken up in methylene chloride and treated with aqueous sodium cyanide and a catalytic amount of tetrabutylammonium bromide according to the procedure of Starks.[27] After ether extraction and drying over magnesium sulfate, the product was distilled to give 46% (based on benzoic-*carboxyl*-^{14}*C* acid) of phenylacetonitrile-α-^{14}*C*, bp 79–80 °C (4 mm).

2-Phenylethyl-*2*-^{14}*C*-amine was obtained by the reduction of phenylacetonitrile-α-^{14}*C* by adding dropwise a solution of lithium aluminum hydride and aluminum chloride to an ether solution of the nitrile. The procedure and workup were essentially the same as described by Nystrom,[28] except that we obtained better yields by adding reducing agent to the nitrile rather than vice versa. The product was obtained in 44% yield, bp 69–70 °C (5 mm).

(2-Phenylethyl-*2*-^{14}*C*)trimethylammonium Iodide. Methyl iodide (2.65 mol) was added dropwise with stirring to 2-phenylethyl-*2*-^{14}*C*-amine (0.33 mol) and tri-*n*-butylamine (0.66 mol) in 500 mL of dimethylformamide.[29] The product precipitated after 3 h and was washed with acetone and recrystallized from ethanol–ether to give 68% of product, mp 233–234 °C (lit.[30] mp 229–230 °C).

Elimination Reactions. The reactions were run to a particular fraction of completion, F, and k_{12}/k_{14} was calculated from eq 4 where R_0 is the molar activity of the original and R is the molar activity of the recovered reactant. Values of F from 0.24 to 0.82 were used, and there was no trend in k_{12}/k_{14} with F for otherwise identical conditions. Most runs used F in the range 0.6–0.8, where the effect on k_{12}/k_{14} of error in F and R/R_0 is least.[31] The exact procedure depended on the speed of the reaction. For relatively slow reactions, the ammonium salt (1.5 g, 0.005 mol) was dissolved in 40–45 mL of Me_2SO–H_2O in a 50-mL volumetric flask such that dilution with the required amount of sodium hydroxide solution

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would give the desired solvent composition. After thermal equilibration, the sodium hydroxide was added, and the reaction was allowed to proceed to the desired degree of completion as calculated from rate data obtained under the same conditions. Where possible the degree of completion was monitored by withdrawing small aliquots, diluting them with ethanol, and measuring absorbance at 248 nm; in highly aqueous media the styrene began to separate at an early stage, and this check could not be employed. The reaction was quenched by cooling to 0 °C and adding sufficient acid to neutralize the remaining base.

For faster reactions, an insufficiency of base was used, and the reaction was allowed to proceed until all of the base was consumed. A control experiment showed no reaction occurs in the absence of base. The ammonium salt (2.0 g, 0.003 mol) was dissolved in ca. 22 mL of solvent in a 25-mL volumetric flask and equilibrated thermally before diluting to the mark with more solvent. Approximately 0.15 mL of concentrated (ca. 23 M) sodium hydroxide was added to the flask and the contents mixed well. The reaction was allowed to proceed until all of the base was consumed, and the concentration of styrene was determined by withdrawing a small aliquot, diluting it with ethanol, and measuring the absorbance at 248 nm. For very fast reactions, there is a danger of error from local depletion of the faster-reacting isotopic species during mixing. Consequently, some of the fastest reactions in 60% Me_2SO were also carried out in a simple rapid-mixing apparatus, a T of stainless-steel tubing of 0.125-in. i.d. with syringes attached vertically to the two ends of the horizontal tube and a receiver flask to the vertical tube. The mixing time for such an apparatus is claimed to be in the range of 10–20 ms.[32] Base solution was placed in one syringe and substrate solution in the other, and the entire apparatus was equilibrated in the constant-temperature bath before the syringe plungers were driven down simultaneously by means of a horizontal connecting bar. The final styrene concentration was determined as above. Results obtained with this apparatus did not differ significantly from those obtained by the conventional mixing procedure, so mixing time was evidently not a source of error in any of our experiments.

For the reactions in ethanol, 1.5 g of substrate was dissolved in 100 mL of dry ethanol and the solution thermally equilibrated. To it was added 10 mL of equilibrated 1.1 M sodium ethoxide solution. At the desired fraction of reaction, three 1.0-mL aliquots were withdrawn and diluted with ethanol to determine the absorbance at 248 nm. The remainder was quenched with hydrochloric acid, cooled in an ice bath, and added to 200 mL of ice-cold ether. The precipitated ammonium salt was removed by suction filtration and dissolved in water for oxidation with potassium permanganate as described below.

The following workup procedure was used in all the reactions in Me_2SO-H_2O. The reaction mixture was poured into 200 mL of distilled water and the solution extracted five times with benzene to remove styrene. A control experiment showed no radioactivity in the benzene extract after the fourth extraction. To the solution was added 2.0 g (0.019 mol) of sodium carbonate, and then potassium permanganate was added cautiously with stirring (a great deal is needed to oxidize both substrate and Me_2SO). Addition was continued until the purple color persisted after 3 h of heating on a steam bath. The solution was cooled and sodium sulfite added to discharge the purple color. Then more sodium sulfite and concentrated hydrochloric acid were added to convert the Mn^{IV} to water-soluble Mn^{II}.[33] The clear solution was cooled and extracted with ether. The extracts were dried over magnesium sulfate, and the ether was removed to yield benzoic acid, which was recrystallized 5–10 times from water. It was dried in vacuo, and ca. 50 mg was dissolved in the scintillation cocktail (15 mL of a solution of 26.5 g of BuPBD in 8 parts of toluene) for activity determination on a Beckman LS-100C liquid scintillation counter. Counting was to the 0.2% (2σ) level of precision, and quench corrections were made by the external standard channels ratio method[34] by using a Beckman standard set of quenched ^{14}C samples to determine the quench correction curve. Counting efficiency was high (ca. 94%) in all cases. Control experiments showed that oxidation of the ammonium salt in water and in 40% Me_2SO gave benzoic acid samples of the same molar activity within 0.1%. The k_{12}/k_{14} values from eq 4 are given in Table I, where each value is the average of two or three separate experiments.

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Activation of Cobalt–Nitro Complexes by Lewis Acids: Catalytic Oxidation of Alcohols by Molecular Oxygen

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Abstract: Lewis acids dramatically enhance the oxidation power of cobalt–nitro complexes. Thus, in the presence of $BF_3 \cdot Et_2O$ or $LiPF_6$, cobalt–nitro complexes such as $pyCo(saloph)NO_2$ or $pyCo(TPP)NO_2$ oxidize primary alcohols to aldehydes and secondary alcohols to ketones. No reaction is observed in the absence of Lewis acids. The effect of Lewis acids is attributed to their association with the nitro ligand, thereby increasing its electrophilicity. The results strongly suggest that the oxidation proceeds via an "ester-like" intermediate, which in a nonradical pathway collapses to the carbonyl product, water, and the corresponding nitrosyl complex. Importantly, it has been found that the reoxidation of the nitrosyl complexes by molecular oxygen is facile in the presence of Lewis acids. This finding facilitated the conversion of the stoichiometric oxidation of alcohols into a catalytic system using molecular oxygen as the oxidant. Initial oxidation rates are rapid. However, the rates decline as the byproduct, water, accumulates in the reaction mixture.

Previously, we advanced a new approach to specific, catalytic oxidations of organic substrates by molecular oxygen.[1] In this approach, the critical step consisted of oxygen atom transfer from a nitro ligand of metal–nitro complexes to organic substrates. This concept (eq 1 and 2) was demonstrated[1] by us in the oxidation

$$M{-}NO_2 + S \rightarrow SO + M{-}NO \qquad (1)$$

$$2M{-}NO + O_2 \rightarrow 2MNO_2 \qquad (2)$$

of triphenylphosphine catalyzed by cobalt–nitro complexes.[2] The importance of this finding lies in the fact that the catalytic cycle exhibits features which are helpful in preventing Haber–Weiss, metal-assisted, nonspecific radical oxidations: (a) The oxidation and reduction occur exclusively at the nitro ligand. (b) The cobalt–nitro and –nitrosyl complexes formally exist in the form of $Co(III){-}NO^-$ and $Co(III){-}NO_2^-$. Thus, the oxidation state

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