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Carbon Isotope Effect during Oxidation of Carbon Monoxide with Nitrogen Dioxide*

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By use of naturally occurring C^{12} and C^{13} isotopes in carbon monoxide, the effect of carbon mass on the rate of the reaction

$$CO+NO_2=CO_2+NO$$

has been studied in a 15-l Vycor flask, in the temperature range 540–727°K, and at pressures between 1 and 20 mm. The rate constant for the reaction was $k=12\times10^{12}\exp(-31{,}600/RT)$ cc mole^{-1} sec^{-1}. The ratio of rate constants k_{12}/k_{13} was 1.022 at 540°K, 1.019 at 638°K, and 1.016 at 727°K. An activated complex was set up with normal bond distances and normal force constants, and with the reaction coordinate explicitly given in terms of internal coordinates with an interaction term such that the restoring force on an antisymmetric stretching symmetry coordinate is reduced to zero. By means of E. B. Wilson's *FG* matrix methods, a vibrational analysis was made of the activated complex, all vibration frequencies were determined for one species, and shifts in frequency due to isotopic substitution were computed by a perturbation method. Similarly, the ratio of effective mass of the reaction coordinate was evaluated, and calculations were checked by the Teller-Redlich product rule. The isotope rate effect was computed by Bigeleisen's formulation of the activated complex theory. For a set of force constants well within the range of normal values and for normal bond radii, calculated isotope rate ratios at all temperatures are in excellent agreement with observed ones.

INTRODUCTION

THE reaction

$$CO+NO_2=CO_2+NO, \quad (1)$$

was found by Crist[1,2] and co-workers to be an elementary bimolecular reaction which occurs at a convenient rate in the temperature range 500–800°. This appeared to be a particularly simple and suitable case for a study of the $C^{12}-C^{13}$ isotope effect on the reaction rate, both because of the clean-cut kinetics and the molecular simplicity of the reactants, making possible a detailed theoretical analysis of the results.

EXPERIMENTAL

Materials

Nitrogen dioxide, obtained from Matheson Company, was treated with oxygen to remove nitric oxide, passed through phosphoric anhydride to remove moisture and repeatedly distilled in vacuum. No impurity could then be found in the nitrogen dioxide by means of infrared analysis; in particular no water, nitric acid, or nitrogen pentoxide was present. Absence of water or nitric acid was essential to this study in order to avoid the chain reaction

$$HO+CO=CO_2+H \quad (2)$$

$$H+NO_2=HO+NO. \quad (3)$$

Carbon monoxide was produced by the action of sulfuric acid on sodium formate, and it was dried and freed of carbon dioxide by passage through Dehydrite and Ascarite towers. Carbon dioxide for the blank runs was prepared by complete combustion of a small sample of the same sodium formate which was used in the preparation of carbon monoxide, using an ordinary analytical semimicro combustion apparatus. Since the $C^{12}-C^{13}$ ratio is quite variable for naturally occurring carbon, it was essential to generate the carbon monoxide for the reactant and blank from the same sodium formate sample.

Apparatus

All runs were made in a 14.5-l Vycor flask which has been fully described elsewhere.[3]

Procedure

The pressures of reactants were measured in gas pipets, and the reactants were passed together into the furnace. All runs were made with a 20-fold excess of carbon monoxide to eliminate errors due to the decomposition of nitrogen dioxide. The reaction was allowed to proceed for a time interval which would allow consumption of less than 1% of the carbon monoxide. The reaction mixture was then pumped through a trap at liquid nitrogen temperature, and the excess carbon monoxide was discarded. The temperature of the trap was raised to −135° (*n*-pentane slush), and the carbon dioxide product was distilled into a bulb at liquid nitrogen temperature. Distillation from −135° to −195° was repeated, and complete separation of carbon dioxide from dinitrogen trioxide and dinitrogen tetroxide was achieved in this way. The pressure and volume of carbon dioxide was measured in order to calculate the rate constant for the over-all reaction. By means of a ratio-recording mass spectrometer the mass ratio 45/44 was determined in order to give the relative rates of reaction of the two isotopes. At the same time the mass ratio 45/44 was determined on the carbon dioxide blank for purposes of comparison. We

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[1] G. M. Calhoun and R. H. Crist, J. Chem. Phys. 5, 301 (1937).

[2] F. B. Brown and R. H. Crist, J. Chem. Phys. 9, 840 (1941).

[3] H. S. Johnston, Discussions Faraday Soc. 17, 1 (1954).

are indebted to Dr. Harold Eding of Stanford Research Institute for our mass spectrometric data.

RESULTS

Duplicate runs were made at each of three temperatures, and duplicate blanks were measured. The concentrations of reactants and the mass ratios are given in Table I.

From the concentrations of reactants and the quantity of carbon dioxide produced, the rate constant for (1) was calculated from the relation

$$d[\mathrm{CO_2}]/dt=k[\mathrm{NO_2}][\mathrm{CO}]. \tag{4}$$

For each isotope of carbon a chemical equation like (1) and a rate expression like (4) may be written. The ratio of these rate expressions gives

$$\frac{d[\mathrm{C^{12}O_2}]}{d[\mathrm{C^{13}O_2}]}=\frac{k_{12}[\mathrm{C^{12}O}]}{k_{13}[\mathrm{C^{13}O}]}. \tag{5}$$

Since less than 1% of the carbon monoxide was allowed to react during each run, the total amount of carbon dioxide produced may be regarded as the initial increment, $d[\mathrm{CO_2}]$, and the isotopic composition of the reactant is essentially unchanged and is given by the blank. Thus one obtains as a good approximation

$$\frac{[\mathrm{C^{12}O_2}]}{[\mathrm{C^{13}O_2}]}=\frac{k_{12}[\mathrm{C^{12}O_2}]_{\mathrm{blank}}}{k_{13}[\mathrm{C^{13}O_2}]_{\mathrm{blank}}}. \tag{6}$$

The isotopic ratio (45/44) was measured directly so that the ratio of rate constants is

$$k_{12}/k_{13}=(45/44)_{\mathrm{blank}}/(45/44). \tag{7}$$

An Arrhenius plot was made of (7) to give the difference in activation energy as

$$E_{12}-E_{13}=-20\pm5\ \mathrm{cal/mole}. \tag{8}$$

An Arrhenius plot was made of k found by (4) to give an energy of activation of 31.6 kcal/mole and a pre-exponential factor $A=12\times10^{12}$ cc mole^{-1} sec^{-1}.

DISCUSSION

Using the notation of Wilson, Decius, and Cross[4] we write down the Teller-Redlich product rule for an activated complex containing N atoms, r free internal rotations, and one reaction coordinate which is essentially a free translation or a vibration with no restoring force.[5]

$$\prod_{k=1}^{3N-7-r}\frac{\omega_k'}{\omega_k}=\prod_{i=1}^{3N}\left(\frac{m_i}{m_i'}\right)^{\frac{1}{2}}\left(\frac{M'}{M}\right)^{\frac{3}{2}}\left(\frac{I_x'I_y'I_z'}{I_xI_yI_z}\right)^{\frac{1}{2}}\times\left(\frac{\mu'}{\mu}\right)^{\frac{1}{2}}\prod_{j=1}^{r}\left(\frac{I_j'}{I_j}\right)^{\frac{1}{2}}, \tag{9}$$

where m is atomic mass, M is mass of the entire complex, and μ is the effective mass of the reaction coordinate, reference 5, pp. 186–189.

Using the partition-function formulation of the activated complex theory[5] for a bimolecular reaction, one gets for the ratio of rate constants for isotopic reactions

$$\frac{k}{k'}=\frac{\kappa}{\kappa'}\frac{Q^{\ddagger}/Q'^{\ddagger}}{Q/Q'}e^{-\Delta\Delta E/RT} \tag{10}$$

where $Q^{\ddagger}$ is the partition function for the activated complex with the contribution due to the reaction coordinate factored out, Q is the complete partition function for the reactant in which isotopic substitution appears, and $\Delta\Delta E$ represents the difference between complex and reactant in the difference of zero point energy, or in this case $(E^0{}_{12}-E^0{}_{13})^{\ddagger}-(E^0{}_{12}-E^0{}_{13})^{\mathrm{CO}}$. The partition-function ratio $Q_1{}^{\ddagger}/Q_2{}^{\ddagger}$ in (10) gives rise to the following product of ratios

$$\left(\frac{\sigma'}{\sigma}\right)_{\ddagger}\left(\frac{M}{M'}\right)_{\ddagger}^{\frac{3}{2}}\left(\frac{I_xI_yI_z}{I_x'I_y'I_z'}\right)_{\ddagger}^{\frac{1}{2}}\times\prod^{r}\left(\frac{I_j}{I_j'}\right)_{\ddagger}^{\frac{1}{2}}\prod^{3N-7-r}\left(\frac{Q_v}{Q_v'}\right)_{\ddagger}, \tag{11}$$

where σ is the symmetry number and Q_v is the partition function for vibrations; there is a comparable expression for the substituted reactant. If Eq. (11) for both complex and reactant is substituted into (9) and (10), the rate expression becomes

$$\frac{k}{k'}=\left(\frac{\mu'}{\mu}\right)^{\frac{1}{2}}\frac{\prod^{3N-7-r}\left[\frac{u(1-e^{-u'})}{u'(1-e^{-u})}e^{\Delta u/2}\right]^{\ddagger}\left(\frac{\sigma'}{\sigma}\right)^{\ddagger}}{\prod^{3n-6}\left[\frac{u(1-e^{-u'})}{u'(1-e^{-u})}e^{\Delta u/2}\right]\left(\frac{\sigma'}{\sigma}\right)}\frac{\kappa}{\kappa'}, \tag{12}$$

where $u=hc\omega/kT$, N is the number of atoms in the complex, n is the number of atoms in the substituted reactant, and the terms in the denominator refer to the substituted reactant. Equation (12), of course, is

TABLE I. Experimental results.

T°K	Reactants m/l×10⁴ CO	NO₂	Mass ratio 45/44×10⁶	k l. mole⁻¹ sec⁻¹	k_{12}/k_{13}
540	5.1	0.35	11 068±9	0.0019	1.0218
541	7.0	0.49	11 050±13	0.0016	1.0225
638	5.8	0.29	11 093±12	0.110	1.0193
638	4.8	0.26	11 071±5	0.120	1.0188
727	5.1	0.29	11 122±14	2.7	1.0157
727	4.6	0.26	11 113±7	3.2	1.0165

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[4] Wilson, Decius, and Cross, *Molecular Vibrations* (McGraw-Hill Book Company, Inc., New York, 1955), p. 184.

[5] Glasstone, Laidler, and Eyring, *Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

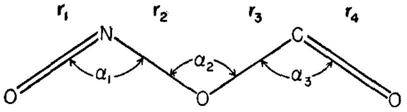

FIG. 1. Structure of the activated complex: $r_1=r_4=1.2$ A; $r_2=r_3=1.4$ A; $\alpha_1=\alpha_2=\alpha_3=120°$; planar.

Bigeleisen's[6,7] expression for the rate ratio for isotopic reactions. The only difference between Eqs. (10) and (12) is the Teller-Redlich product rule (compare reference 7, footnote 2). Whether one uses (10) or (12) depends on whether one had rather compute moments of inertia (including those for internal rotation) or mass ratio along the reaction coordinate. [Actually it is desirable to compute both sets of quantities to substitute into (9) as a check against computational errors.] Bigeleisen's formulation is considerably more convenient for computational purposes in the present case.

To use Eq. (12) one needs the mass ratio μ/μ' and the vibration frequencies for unsubstituted and substituted reactant and activated complex. These quantities are readily obtained by means of Wilson's F and G matrices,[4] provided one has a model of the activated complex. For this reaction we use the model previously proposed[8] with certain minor refinements. The activated complex was assumed to be of the planar dinitrogen trioxide structure, Fig. 1, with bond angles of 120°. The double-bond distances, 1.2 A, were taken as the sum of the double-bond radii of the elements, and the single bond distances, 1.4 A, were taken from single bond radii.[9] Partition functions for translation, rotation, and internal rotation were calculated from this model. For the vibrational analysis, a slight change was introduced in order to increase the symmetry of the unsubstituted activated complex and thus greatly simplify the calculations. The actual masses of the atoms in the activated complexes are 16–12–16–14–16 and 16–13–16–14–16. The first of these was replaced by the average-mass case 16–13–16–13–16, and the second was retained. Thus the unsubstituted complex had C_{2v} symmetry and the substituted complex was treated by a perturbation method.[10]

Force constants were assigned by analogy[11] and by use of Badger's rule.[12] Ratios of force constants were assigned as: 2, double bond stretch to single bond stretch; 10, single bond stretch to end k_α/r_1r_2; 2, end bend to center bend.[13] The magnitude of the single bond stretching force constant is 5×10^5 dynes/cm according to Badger's rule; by analogy with C−C, O−O, N−N, C−N, and C−O single-bond force constants,[11] the range $3\frac{1}{2}\times10^5$ to 6×10^5 appears to be very reasonable (we have made calculations for the values of 4, 5 and 6×10^5). The reaction coordinate was treated as before[8]; an interaction constant was introduced which reduces to zero the restoring force on the antisymmetric stretching mode involving the central oxygen atom

$$2V=k_s(r_2^2+r_3^2)+2k_s'r_2r_3+\text{other square terms.} \tag{13}$$

As k_s' approaches k_s the restoring force of the antisymmetric center stretch goes to zero, and the reaction coordinate becomes separated from the normal modes of vibration.

Out-of-plane motions for this complex are the internal rotations. A rough estimate of the barrier to internal rotation[14] indicates it to be less than RT for this complex. Thus computations are made on the assumption of free internal rotation.

With this model for the activated complex the F and G matrices[4] were set up in the usual way. The seven-by-seven FG matrix reduces to a four-by-four (A_1) and a three-by-three (B_2) which includes the reaction coordinate with zero frequency. The six nonzero frequencies and the corresponding normal modes with their normalized *eigenvectors* were found; then the shifts in frequency caused by a single isotopic substitution in the activated complex were computed by a perturbation method.[10] These frequencies and their shifts are given in Table II.

The "effective mass" along the reaction coordinate is readily calculated as a by-product of the normal-mode analysis. For the terms in (13) let $k_s'-k_s$ be ϵ, a number as close to zero as desired. The corresponding λ is so low that terms in λ^2 and higher may be neglected. In terms of F and G determinants the value of λ is[15]

$$\lambda=|G|\,|F|/\Sigma G^{(2)}F^{(2)}, \tag{14}$$

TABLE II. Contribution of the various normal modes of vibration to the various rate factors. Q contributes to A, Q_{12}/Q_{13} contributes to k_{12}/k_{13}, and $E_{12}-E_{13}$ is given directly. T is 638°K. Force constants are 8–4–0.4–0.2.

Normal Mode	$\omega_{\text{cm}^{-1}}$	Q	$\Delta\omega^a$ cm^{-1}	$-\ln\frac{Q_{12}}{Q_{13}}$	$E_{12}-E_{13}$, cal/mole ΔE^0	$RT\theta^b$
Sym. str., mid.	1160	1.08	12.4	0.0022	17.8	−5.1
Sym. str., end	1495	1.04	12.4	0.0010	17.8	−3.2
Sym. bend, end	335	1.88	1.3	0.0027	1.9	−1.4
Mid bend	176	3.05	1.2	0.0054	1.7	−1.4
React. coord.						
Anti. sym. str., ends	1381	1.05	13.8	0.0015	19.7	−4.3
Anti. sym. bend	451	1.57	4.9	0.0063	7.0	−4.8
CO	2169	1.01	49.2	0.0008	70	−4.1
			E calc		−20.2	
			E obs		−20±5	

[a] This is a decrease in all cases.
[b] $\theta=d\ln Q/d\ln T$.

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[6] J. Bigeleisen, J. Chem. Phys. **17**, 675 (1949).

[7] J. Bigeleisen and M. G. Mayer, J. Chem. Phys. **15**, 261 (1947).

[8] Herschbach, Johnston, Powell, and Pitzer, J. Chem. Phys. **25**, 736 (1956).

[9] Linus Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1940).

[10] See reference 4, p. 188.

[11] See reference 4, pp. 175–176.

[12] R. M. Badger, J. Chem. Phys. **2**, 129 (1934); **3**, 710 (1935).

[13] These ratios are based on reference 11 and on analogy to nitrogen tetroxide and to ethers. Other ratios could be used within the range of examples from normal molecules.

[14] E. A. Mason and M. M. Kreevoy, J. Am. Chem. Soc. **77**, 5808 (1955).

[15] See reference 4, p. 68.

TABLE III. Calculated rate factors as a function of variation of force constants assumed for the activated complex.

Force constants dynes cm^{-1} ×10^{-5}				k_{12}/k_{13}				
End Str.	Mid Str.	End bend	Mid bend	540°	638°	727°	$E_{12}-E_{13}$ cal/mole	$A\times10^{-12}$ cc m^{-1} sec^{-1} 638°[a]
8	4	0.4	0.2	1.0208	1.0180	1.0160	−20	26
10	5	0.5	0.25	1.0138	1.0124	1.0113	−10	20
12	6	0.6	0.3	1.0097	1.0092	1.0090	−3	14
observed				1.0221	1.0190	1.0161	−20±5	12

[a] Based on unity for kappa.

where $G^{(2)}$ is any two-rowed minor of $|G|$ and $F^{(2)}$ is the corresponding two-rowed minor of $|F|$, summed over all such minors.[15] For the isotopically substituted complex the expression is

$$\lambda'=|G'||F|/\Sigma G'^{(2)}F^{(2)}. \tag{15}$$

The ratio of these two terms leads to cancellation of $|F|$, and it is the ratio of effective masses μ

$$\lambda/\lambda'=\mu'/\mu. \tag{16}$$

Now, as one lets $k_s'=k_s$, some terms in $F^{(2)}$ go to zero and some others cancel out. For the present case (the reaction coordinate is number 5, the antisymmetric end stretch is 6, and the antisymmetric end bend is 7) the expression for the ratio of masses is

$$\frac{\mu}{\mu'}=\frac{|G'|}{|G|}\,\frac{G_{6,7}{}^{(2)}}{G'_{6,7}{}^{(2)}}, \tag{17}$$

where $G'=G+\Delta G$. The changes in G, that is, ΔG, were used in the perturbation method calculation. In (17) $|G|$ is the complete three-by-three (B_2) determinant. For the present case the value of μ_{13}/μ_{12} was 1.0095.

By the use of this value of μ'/μ and (9), a check can be made against the six planar vibration frequencies. The product of the ratio of vibration frequencies is 1.0521; the product of the ratios of atomic weights, molecular weights, one moment of inertia, and μ/μ' on the right-hand side of (9) is 1.0510. The discrepancy of 0.001 is believed to be a measure of the validity of the perturbation method for this case; it might be noted that this discrepancy is by no means negligible.

Rate constant ratios were computed[16] for three sets of force constants: 8–4–0.4–0.2, 10–5–0.5–0.25, and 12–6–0.6–0.3. The calculated curve for k_{12}/k_{13} is plotted against $1000/T$ in Fig. 2. The force constants 8–4–0.4–0.2 give a curve lying very close to the observed points at all temperatures; the other two curves miss the points and have the wrong temperature dependence. The calculated curves are very sensitive to small changes in the assigned force constants; obviously a small reduction in the lowest set of force constants would give almost perfect agreement with experiment. This adjustment is unnecessary. The primary point established is that this simple method[8] of setting up and characterizing the activated complex and reaction coordinate gives a good description of the isotope rate effect within the limits of a normal set of bond distances and force constants. In the calibration of this method of constructing activated complexes, it might be noted that the pre-exponential factor is particularly sensitive to low frequency oscillators and free internal rotations. On the other hand, these quantities have little or no effect on the isotope rate factors k/k', and $E-E'$. The high-frequency oscillators are by far the most important contributors to the isotope rate effect; this point has been made by Bigeleisen.[6] The contribution of the various frequencies to k/k' and $E-E'$ is given in Table II. A comparison of the different sets of force constants for the rate factors, A, k/k', and $E-E'$ is given in Table III. The agreement between calculated and observed pre-exponential factor is quite satisfactory for all choices of the force constants (a factor of two is precise agreement here and a factor of 10 is within experimental error).

Finally, we wish to give a short discussion emphasizing the distinction between the isotope effect contributed by the reaction coordinate and the isotope

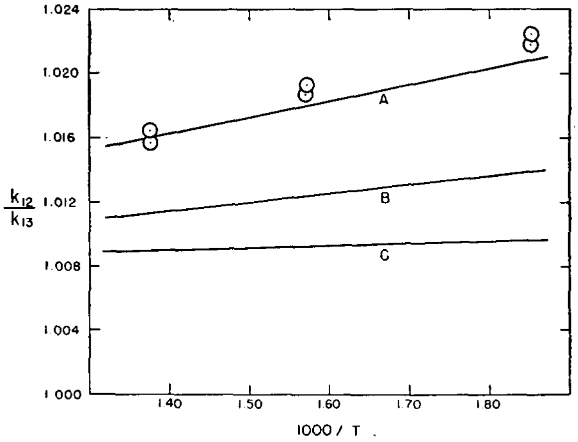

FIG. 2. Calculated curves and observed points for the isotope rate effect at various temperatures. The force constants for end-stretch: mid-stretch: end-bend: mid-bend are respectively: A, 8–4–0.4–0.2; B, 10–5–0.5–0.25; C, 12–6–0.6–0.3 in units of 10^5 dynes/cm.

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[16] Bigeleisen and Mayer[7] give extensive tables of a function they call $G(u)$. This function employs the approximation, $e^{\Delta u/2}=1+\Delta u/2$. Because of the very small isotope effect observed here, we found this approximation to be extremely poor for this case. In making these computations we kept all figures to six significant figures, rounding off only at the end. Unless extreme care is taken in these computations, rounding-off errors can easily become as large as the isotope effect itself.

In these calculations the ratio of kappas was taken as one.

effect contributed by the rest of the activated complex. In terms of Bigeleisen's formulation the reaction coordinate contributes $(\mu/\mu')^{\frac{1}{2}}$ toward the isotope effect, and that is all (actually this treatment neglects the possibility of a very narrow δ, width of the top of the barrier to the reaction coordinate, and thus a significant zero-point energy in the reaction coordinate itself). The other normal modes in the activated complex contribute their product of u_i, their product of Q_i, and the zero-point energy difference, $\Sigma h\nu_i/2$. Thus isotopic substitution in atoms removed from the site of the reaction coordinate, could lead to an isotope rate effect. For the present reaction an isotope effect should be observed between CO^{16} and CO^{18}, for example.

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Rate Constants of Second-Order Reactions from Kinetic Current Measurements

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Kinetic currents have been calculated for the case where the solution contains two electroactive species, one of which may undergo a second order reaction with the reduced form of the other. The results have been applied to the reaction between ferrous versenate and cumene hydroperoxide, assuming the diffusion coefficients of all species to be equal. The calculated and observed rate constants are found to differ by 33%, which constitutes reasonable agreement in view of the assumptions made.

DELAHAY[1] has recently written a monograph which reviews the mathematical treatment of kinetic and catalytic currents for many systems in considerable detail. In these systems the current which results from the oxidation or reduction of a substance at an electrode is controlled partly by diffusion of the electroactive species to the electrode and partly by the formation or consumption of the electroactive species in a chemical reaction. An example of this type of system, which has not yet been treated quantitatively, is obtained when solutions of ferric versenate (O) and cumene hydroperoxide (Z) are mixed and reduced at a dropping mercury electrode. Both species yield reduction currents over the whole range of available electrode potentials and hence neither one can be selectively reduced in the presence of the other. Ferric versenate is reduced, at the electrode, to ferrous versenate (R). As R diffuses away from the electrode it reacts with Z, diffusing toward the electrode to produce O and a reduced form Y' of the hydroperoxide, probably acetophenone.[2] Hydroperoxide is reduced at the electrode to Y, probably phenyldimethylcarbinol and water, since the reduction is a two-electron reduction. Neither acetophenone nor phenyldimethylcarbinol reacts further unless an electrode potential more negative than −1.5 volt (*vs* saturated calomel electrode) is used, in which case acetophenone will be reduced. The general reaction scheme is thus

$$Z+me\rightarrow Y \quad \text{(at electrode)} \tag{1}$$

$$O+ne\rightarrow R \quad \text{(at electrode)} \tag{2}$$

$$R+Z\rightarrow Y'+O \quad \text{(in solution).} \tag{3}$$

The equation for the instantaneous current resulting from reduction of Z at the electrode is

$$i_Z=n_ZaFD_Z\left(\frac{\partial C_Z}{\partial x}\right)_{x=0}, \tag{4}$$

and that from reduction of O is

$$i_O=n_OaFD_O\left(\frac{\partial C_O}{\partial x}\right)_{x=0}, \tag{5}$$

where F is the Faraday constant, n_Z and n_O the number of faradays involved per mole of Z and O reduced, a the area of the electrode at time t, D_Z and D_O the diffusion coefficients of the indicated species, and $(\partial C_Z/\partial x)_{x=0}$ and $(\partial C_O/\partial x)_{x=0}$ the concentration gradients of Z and O at the electrode surface at time t. The total instantaneous current is

$$i_t=i_Z+i_O. \tag{6}$$

The average total current in the case of the dropping mercury electrode is obtained by expressing the area, a, and the concentration gradients at $x=0$ as functions of time, averaging over the drop time of the electrode, and then multiplying by the factor $(7/3)^{\frac{1}{2}}$, which has been used to convert results obtained for plane electrodes to results for spherical electrodes.[3] The factor $(7/3)^{\frac{1}{2}}$ is an empirical factor which corrects for the nonplanar surface of the electrode and for the movement of the growing drop.

The average total current differs, in general, when reaction between R and Z occurs and when reaction between R and Z does not occur. This difference is

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[1] Delahay, *New Instrumental Methods in Electrochemistry* (Interscience Publishers Inc., New York, 1954).

[2] W. L. Reynolds and I. M. Kolthoff, J. Phys. Chem. **60**, 996 (1956).

[3] P. Delahay and G. L. Stiehl, J. Am. Chem. Soc. **74**, 3500 (1952).