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Rate Constants for the Reactions $tC_4H_9 + DX \rightarrow iC_4H_9D + X$ ($X = Br, I$), $295 T(K) < 384$: Heat of Formation of the tertButyl Radical

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an orientation matrix for data collection were obtained from least-squares refinement, by using the setting angles of 25 reflections in the range $12^\circ < |2\theta| < 15^\circ$, yielding the cell parameters given in Table II. From the systematic absences of $h k 0$, $h = 2n$; $h 0 l$, $l = 2n$; $0 k l$, $k = 2n$ and subsequent least-squares refinement, the space group was determined to be *Pbca* (no. 61). Moving-crystal moving-counter background counts were made by scanning an additional 25% above and below this range. Thus the ratio of peak counting time to background counting time was 2:1. The counter aperture was 3.0 mm wide by 4.0 mm high. The diameter of the incident beam collimator was 1.5 mm, and the crystal to detector distance was 21 cm.

A total of 12 777 reflections ($+h, +k, +l$) were collected, of which 5735 were unique and not systematically absent. As a check on crystal and electronic stability, four representative reflections were measured every 60 m of X-ray exposure. A total loss in intensity of 5.0% was observed and a linear decay correction was applied. The correction factors on I ranged from 1.000 to 1.026 with an average value of 1.011. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 7.0 cm^{-1} for Mo K(α) radiation. ψ scans of five reflections with θ between 4.45 and 14.66° showed small variations in intensity. No absorption correction was made, the largest error left untreated thereby being approximately 2% on I . Intensities of equivalent reflections were averaged. The agreement factors for the averaging of the 5269 observed and accepted reflections was 2.7% based on intensity and 2.4% based on F_o . (Eleven reflections were rejected from the averaging statistics because their intensities differed significantly from their average. This was due to large ratios of $I/\sigma(I)$.)

The structure was solved by direct methods by using the data up to $\sin \theta/\lambda = 0.478$ (0.4 of a copper sphere). Using 319 reflections (minimum E of 1.50) and 12 655 relationships, a total of 21 phase sets were produced. The cobalt ion was located from an E-map prepared from the phase set with probability statistics: absolute figure of merit = 1.32, residual = 14.45, and $\phi_0 = 2.291$. No other atoms were discerned in this E-map, but the cobalt position was confirmed by a Patterson map. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atom positions were calculated and then added to the structure factor calculations, but their positions were not refined. The position of the hydrogen atom bonding to the boron was taken from a persistent difference peak. The structure was refined in full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$, and the weight w is defined as: $w = 4F_o^2/\sigma^2(F_o^2) = 1/\sigma^2(F_o)$. The standard deviation on

intensities, $\sigma(F_o^2)$, is defined as $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/Lp^2$, where S is the scan rate, C is the total integrated peak count, Lp is the Lorentz-polarization factor, and the parameter p is a factor introduced to downweight intense reflections. Here p was set to 0.040.

Scattering factors were taken from Cromer and Waber.⁴⁶ Anomalous dispersion effects were included in F_c ,⁴⁷ the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.⁴⁸ Only the 3106 reflections having intensities greater than 2.0 times their standard deviation were used in the refinements. The final cycle of refinement included 316 variable parameters and converged with unweighted and weighted agreement factors of $R_1 = \sum |F_o - F_c|/\sum |F_o| = 0.037$ and $R_2 = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{0.5} = 0.040$. The standard deviation of an observation of unit weight was 1.04. There were no correlation coefficients greater than 0.50. The final difference Fourier map was judged to be featureless. Plots of $\sum w(|F_o| - |F_c|)^2$ vs $|F_o|$, reflection order in data collection, $\sin(\theta)/\lambda$, and various classes of indices showed no unusual trends. Final positional parameters are given in Table III, and thermal parameters appear in the Supplementary Material.

Acknowledgment. We are grateful for the support of the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, as well as the contributions of D. B. Palladino and J. Feilong to early and related studies, respectively. The support of the DAAD and the hospitality of Prof. Dr. W. Siebert at Heidelberg where the seeds of these ideas were planted are also gratefully acknowledged. We thank Prof. T. A. Albright for information in advance of publication and appreciate the comments of a referee.

Supplementary Material Available: Listing of thermal parameters and hydrogen atom positions and the packing diagram (6 pages); listing of observed and calculated structure factor amplitudes (29 pages). Ordering information is given on any current masthead page.

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(47) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(48) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, GB, Vol. IV, 1974; Table 2.3.1.

Rate Constants for the Reactions $t\text{-C}_4\text{H}_9 + \text{DX} \rightarrow i\text{-C}_4\text{H}_9\text{D} + \text{X}$ ($\text{X} = \text{Br}, \text{I}$), $295 < T \text{ (K)} < 384$: Heat of Formation of the *tert*-Butyl Radical

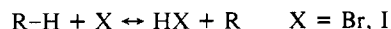
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Contribution from the Department of Chemical Kinetics, Chemical Physics Laboratory, SRI International, Menlo Park, California 94025. Received May 23, 1988

Abstract: Absolute values for the rate constants of the metathesis reactions of DX ($\text{X} = \text{Br}, \text{I}$) with *tert*-butyl, generated by 351-nm photolysis of 2,2'-azoisobutane, were determined in a low-pressure Knudsen cell reactor using the VLP Φ (very low pressure photolysis) technique. For $\text{X} = \text{Br}$, the values are $10^{-8}k \text{ (M}^{-1} \text{s}^{-1}) = 0.9$ and 2.3, and for $\text{X} = \text{I}$ the values are 2.1 and 3.1 at 295 and 384 K. The latter are in good agreement with earlier measurements from this laboratory. The former values are lower by a factor of 50 compared to those recently reported at 295 K and fail to show the negative activation energy found in that work. Correcting by $\sqrt{2}$ for the primary isotope effect and combining with the rate constants for the reverse reactions lead to $\Delta H_f^\circ(298)(\text{tert-butyl}) \text{ (kcal mol}^{-1}) = 9.2 \pm 0.5$ in both cases. First-order heterogeneous loss of *tert*-butyl radicals on the Teflon-coated surface employed is small ($< 2 \text{ s}^{-1}$).

The importance of knowledge of thermochemical data for *tert*-butyl radicals and other prototypical radicals (e.g., *i*-propyl, ethyl, and methyl) has been addressed by many authors in the past.¹⁻⁵ The persisting discrepancies between data derived from

different types of kinetic studies, e.g., from iodination/bromination investigations^{3,4,6-8}



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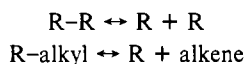
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(3) Rossi, M. J.; Golden, D. M. *Int. J. Chem. Kinet.* **1983**, *15*, 1283.

(4) Rossi, M. J.; Golden, D. M. *Int. J. Chem. Kinet.* **1979**, *11*, 969.

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or, on the other hand, from bond scission and recombination processes of simple alkanes or free radicals.^{5,9-11}



These reactions have been discussed extensively. Since the consequences concerning the primary, secondary, and tertiary C-H bond energies have been pointed out elsewhere,^{2,3,12} we proceed directly to the discussion of very recent reports by Russell et al.¹ They report the results of a new investigation of the reaction



and of the reverse reaction (B).

Reaction A has been studied by means of a tubular flow reactor, coupled to a photoionization mass spectrometer, in the temperature range from 296 to 532 K. *tert*-Butyl radicals were prepared by photolysis of 4,4-dimethyl-1-pentene or 2,2,4,4-tetramethyl-3-pentanone using the 193-nm radiation of an excimer laser. The radicals were then allowed to react with HBr. The ion signals due to *tert*-butyl radicals were recorded as a function of time by means of the photoionization mass spectrometer.

Reaction B was investigated separately between 533 and 710 K in the same experimental setup, using CF₂Br₂ as a source of Br atoms. In addition, the authors have studied reaction B in the temperature range 298–478 K using a temperature-controlled flash-photolysis apparatus with resonance fluorescence detection of Br atom time profiles. Bromine atoms were produced via the flash photolysis of CHBr₃ at $\lambda > 190$ nm and allowed to react with isobutane. Temperature dependence of both, the forward (A) and the reverse (B) reaction are reported, which enabled the authors to perform a second-law determination of the heat of formation of *tert*-butyl radicals.

Although the rate constant obtained for reaction B is somewhat larger than the recent values of Benson, Kondo, and Marshall,⁷ who employed VLPR techniques, this result basically does not contain any surprises.

The opposite holds for the reported rate constant for the forward reaction (A). A negative activation energy of -1.4 ± 0.2 kcal mol⁻¹ has been found, which implies a "large" value for $\Delta H_f^\circ(298\text{K})(t\text{-C}_4\text{H}_9)$ of 11.6 kcal mol⁻¹, close to that determined in the bond scission studies⁹⁻¹¹ and in distinct contradiction to the result of the DI + *t*-C₄H₉ metathesis VLPΦ study of Rossi and Golden³ ($\Delta H_f^\circ(298\text{K})(t\text{-C}_4\text{H}_9) = 9.2$ kcal mol⁻¹) and the work of Benson and co-workers.^{6,7} Since the negative activation energy is without precedence for this class of reactions, a complex mechanism involving a bound intermediate between the radical and DBr is proposed by Russell et al.

The uncertainty in the rate constant of reaction B cannot account for the disparities between the results of ref 1 and ref 3, 6, and 7. Furthermore, since the value of the entropy of *tert*-butyl radicals is well established,^{13,14} only three explanations of these contradictions come easily to mind:

- (i) The measured rate constant for the DI analogue of reaction A in the VLPΦ study of Rossi and Golden is by far too slow, especially at ambient temperatures (approximately a factor of 50). The reason for this might be an undetected large contribution from a first-order wall loss (of *tert*-butyl radicals) to the overall observation. Reasonable suggestions about the possible effect of processes like this are included in ref 1 (Russell et al.). If this were true, the "high" value of $\Delta H_f^\circ(298\text{K})(t\text{-C}_4\text{H}_9)$ would be correct.
- (ii) An unexpectedly large change in the activation energy between the HBr + *tert*-butyl system and the corresponding

Table I. Important Parameters of the VLPΦ-Knudsen Reactor^a

<i>n</i>	inner diameter, mm	<i>C</i>
1	1.0	0.213
2	1.5	0.469
3	2.0	0.730
4	3.3	1.825
irradiation section length, cm		22.6
irradiation section inner diameter, cm		2.54
total volume, cm ³		162.8

^a Escape rate constants are given in the form $k_{e,n} = C(T/M)^{1/2} s^{-1}$ where T = absolute temperature (K), M = molar mass (amu), and n = aperture number.

HI/DI + *tert*-butyl reaction system occurs. In this case, several possibilities may be obtained. If the "low" value for the heat of formation of *tert*-butyl radicals from ref 3 is correct, then the accepted knowledge about reaction B must be erroneous if the rate parameters for reaction A of Russell et al. are accepted. On the other hand, if the large value of $\Delta H_f^\circ(298\text{K})(t\text{-C}_4\text{H}_9)$ is correct and point (i) above does not apply, this is, if the rate parameters of Rossi and Golden³ are correct, then the kinetic parameters of the reverse reaction in the HI + *t*-C₄H₉ system (Bracey and Walsh⁸) are incorrect. However, since the rate parameters from halogenation experiments, such as reaction B and its I analogue (iodination kinetics), have generally been found to be accurate, we are left with the simple alternative that a low value for $\Delta H_f^\circ(298\text{K})(t\text{-C}_4\text{H}_9)$ is consistent with the rate parameters of ref 3, whereas a high value results from rate parameters measured in ref 1. Therefore, the choice between low and high values for $\Delta H_f^\circ(298\text{K})(t\text{-C}_4\text{H}_9)$ depends directly on whether the rate parameters for reaction A and its DI/HI analogue are similar (expected) or significantly different (unexpected). Furthermore, the residual uncertainty in $S^\circ(298\text{K})(t\text{-C}_4\text{H}_9)$ may still contribute to the controversial situation to some extent.

(iii) The rate constant for the reaction A from ref 1 is inaccurate for unknown reasons.

In the following we present a new investigation of reaction A and its HI/DI analogue, in which we address the problems mentioned above and establish the similarity of the rate parameters between the I and Br systems. The present work should be understood in direct conjunction with the earlier study of the DI/HI + *tert*-butyl metathesis reaction^{3,4} but addresses the problem of separation of the reaction of interest from possible wall contributions. Our aim was to "overdetermine" the heat of formation of *tert*-butyl radicals by investigating the metathesis reaction of *tert*-butyl radicals with deuterium bromide in addition to reinvestigating the previously studied corresponding deuterium iodide reaction, since both reverse reaction rate constants are known. The results of the present work support the low value for the standard heat of formation of the *t*-C₄H₉ free radical.

Experimental Section

A full description of the entire very low pressure photolysis (VLPΦ) apparatus has been given in a previous publication;³ therefore, only a brief description is given here, focusing upon recent modifications.

The Knudsen reactor was equipped with interchangeable apertures that allowed us to perform measurements of the reaction of *tert*-butyl radicals with DI or DBr at a total of four different escape rate constants. The irradiation of the Teflon-coated, all quartz, reaction vessel allowed the preparation of *tert*-butyl radicals by photolysis of 2,2'-azoisobutane using 351-nm light pulses from a XeF excimer laser (Lumonics TE-860-3).

Two separate inlet capillary systems were used to control the flow of the radical precursor and the radical titrant (DBr or DI) into the reactor, such that even at the highest flow rates Knudsen conditions were maintained. When a calibrated pressure transducer (Validyne DP 15) was used, flow rates were determined by monitoring the pressure drop as a function of time in a calibrated volume.

Reactants and products leaving the Knudsen cell were formed into an effusive molecular beam penetrating into the ion source of a quadrupole mass spectrometer (Balzers QMG 311) after passing two differentially pumped vacuum chambers (Turbo-molecular pumps Pfeiffer/Balzers TPH 270 and TPH 110, respectively). Modulating the molecular beam

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by means of a tuning fork (150 Hz) allowed phase-sensitive detection of the total ion current using a lock-in amplifier (Stanford Research Systems SR 510).

The reaction vessel was characterized by the parameters summarized in Table I. The calibration of the escape rate constants for the different apertures was performed by means of an absolute pressure gauge (Baratron HA 227 A-1). The absolute pressure in the Knudsen cell was measured as a function of the flow rate of $i\text{-C}_4\text{H}_{10}$ into the reactor. The escape rates thus obtained are in excellent agreement with the values calculated on the basis of the geometry of the reactor and the sizes of the apertures.

The entire reactor was wrapped with heating tape in order to perform measurements at elevated temperatures. At ~ 400 K, a reasonably uniform temperature distribution could be achieved by additional heating of the Viton Q-ring sealed Suprasil windows (Heraeus Amersil), by using a regulated hot air gun. Temperature was measured at several positions with thermocouples.

The actual measurements were performed by monitoring the ion current due to the reaction product $i\text{-C}_4\text{H}_9\text{D}$ at $m/e = 44$ as a function of the flow rate of the titrant (DBr or DI) into the Knudsen cell with as many different escape apertures as possible. Mass spectral sensitivity was taken to be identical with that of $m/e = 43$ in $i\text{-C}_4\text{H}_{10}$; however, the rate constant determination does not rely on an absolute calibration of the mass spectrometric signals of isobutane- d_1 .

A steady-state concentration of *tert*-butyl radicals was provided by 351-nm photolysis of 2,2'-azoisobutane at laser repetition frequencies such that the period between two subsequent laser pulses was short compared with the residence time of the radicals in the reactor. The extent of photolysis ranged from a fraction of a percent to 2%. The transmitted laser power was recorded simultaneously by a power meter (Scientech 362) located behind the irradiation section of the Knudsen cell. All signals were normalized for constant transmitted power.

Since isotope exchange reactions take place in the inlet capillary system, the ratio of DBr/HBr of DI/HI was determined separately for every single flow rate of the titrant, so that it was possible to convert the measured total flow into an effective flow of the deuterated species. 2,2'-Azoisobutane (Fairfield Chemical Co.), deuterium iodide (Merck, Sharp, Dohme, Ltd., Canada [d_1 , 99%]), and deuterium bromide (CIL, [d_1 , 99%]) were purified by trap-to-trap distillation. As an example, the escape rate constant specified above for the 2-mm aperture (no. 3) translates into a partial pressure of the titrant DBr of 0.66 mTorr at a flow rate into the reactor of $F_{\text{DBr}} = 5 \times 10^{15} \text{ s}^{-1}$.

Results and Discussion

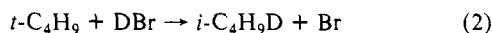
In previous VLP Φ studies of the reaction



kinetic data were reported for only one escape rate constant (ref 3; "small aperture"), because the extent of reaction 1 using the larger aperture turned out to be quite small for the range of flow rates corresponding to Knudsen flow conditions. (In fact, the small aperture in each of two reactors was used. These corresponded roughly to apertures 2 and 3 of the current reactor, so multiple aperture experiments have really already been performed!)

It is desirable, however, to measure the rate constant for reaction 1 independently at a fixed temperature with several different escape apertures. This procedure leads to an overdetermined kinetic system that will allow the assessment of the contribution of any heterogeneous reactions to the simple homogeneous reaction scheme, which consists merely of reaction 1 and the escape of all species involved, that is used by Rossi and Golden.^{3,4} If a systematic trend is found in the independently determined rate constants, measured with different escape apertures, this could indicate a nonnegligible contribution from heterogeneous effects. This should then allow us to decide whether previous VLP Φ studies of k_1 may have consisted of a combination of homogeneous and heterogeneous processes. Hopefully, this would clarify the origin of the discrepancies between the recent work of Russel et al. and the VLPP/VLP Φ studies of Rossi and Golden.^{3,4}

Furthermore, it is the goal of the present work to provide measured values for the rate constant of the reaction



in order to facilitate a direct comparison with the recent work of Russell et al. (after trivial correction for the primary isotope effect).

The new determination of k_2 , combined with the measurements of the reverse reaction reported by Russell et al.,¹ will also provide

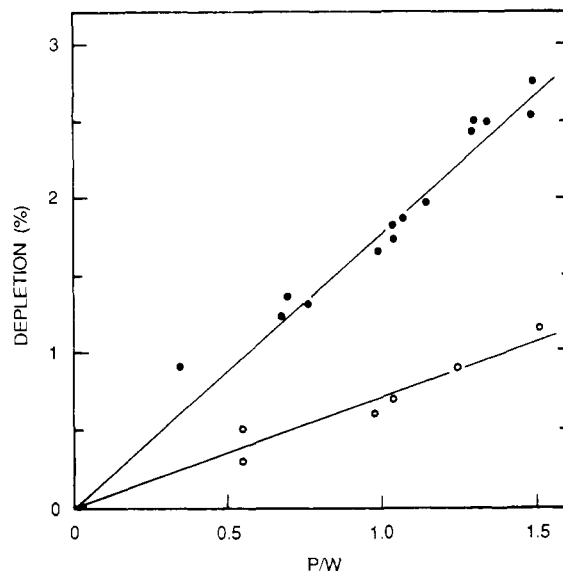


Figure 1. Depletion of 2,2'-azoisobutane as a function of transmitted laser power at 351 nm, measured at $m/e = 57$. Aperture diameter: ●, 2 mm; ○, 3.2 mm. Flow rate of azoisobutane into the reactor F_{AZO} of $3 \times 10^{15} \leq F_{\text{AZO}} \leq 1.2 \times 10^{16} \text{ s}^{-1}$.

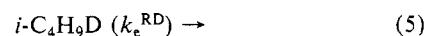
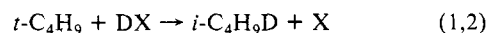
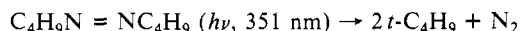
additional access to the standard heat of formation of *tert*-butyl radicals. It will answer the question of whether an unexpectedly big change in the rate constants of the DBr reaction takes place, compared to the analogous DI reaction.

Figure 1 shows the percentage of depletion of the azo compound as a function of the transmitted laser power at 351 nm, measured at the marker peak for the parent molecule, $m/e = 57$. The *tert*-butyl radical does not contribute to this mass peak given the disparate densities of the radical and its precursor. The depletion scales linearly with the transmitted laser power, within the experimental error limits indicated in Figure 1. Since the amount of depletion of the radical precursor was fairly small compared to the analogous thermal (VLPP)⁴ experiments ($\sim 1\%$), it was not possible to derive undisputed values for the recombination rate of two *tert*-butyl radicals at room temperature. Even so, at flow rates of $\sim 10^{16}$ molecules/s, a $m/e = 99$ signal indicative of 2,2,3,3-tetramethylbutane was obtained. This is one of many indications (vide infra) that *tert*-butyl radicals are not lost at the walls of the reactor at a significant rate compared with escape.

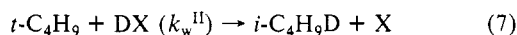
As an important point, it should be reported here that the recombination product mass peak ($m/e = 99$) vanishes totally at DBr or DI flow rates larger than 1.5×10^{15} molecules/s, indicating that the recombination is unimportant under titration conditions. The lowest flow rates of DBr (or DI) used in these experiments were $\sim 3 \times 10^{14}$ molecules s^{-1} . Even at these low flows we find that recombination is negligible. (Measured flows of the recombination product are on the order of 5×10^{10} molecules s^{-1} when isobutane- d_1 flows are on the order of 5×10^{13} molecules s^{-1} .) As pointed out in the previous study,³ similar arguments apply for the importance of the homogeneous disproportionation of *tert*-butyl radicals into isobutane and isobutene in the presence of the titrant.

The influence of wall-catalyzed processes, however, remains uncertain to some extent, unless data observed in an overdetermined system are taken into account. Therefore the overall reaction scheme should be considered as follows ($X = \text{I}, \text{Br}$):

Homogeneous



Possibly Heterogeneous



The isobutane- d_1 formed is monitored at $m/e = 44$ at a constant flow rate of the azo precursor as a function of the flow rate of DI or DBr (Figure 2) and shows that the mass spectrometric signal at $m/e = 44$ at a fixed flow rate of 2,2'-azoisobutane and DBr is a linear function of the transmitted laser power; the ratio of the slopes of the given curves represents the ratio of the escape rate constants for the two apertures used in this example.

A typical experimental observation is shown in Figure 3. The mass spectrometric trace was recorded during continuous irradiation with 351-nm light pulses at 60 Hz. The indicated flow rate of DBr is the corrected value using the ratio of the mass peaks at $m/e = 83$ and $m/e = 82$, according to the ratio of DBr to HBr mass spectral sensitivities. (The related mass spectrum around mass 80 is included in Figure 3.)

Three observations are of importance: First, there is no dark reaction between 2,2'-azoisobutane and DBr in contrast to the reaction of 2,2'-azoisobutane with DI,³ in which case, we were precluded from studying this reaction at temperatures in excess of 400 K due to increasing interference of the dark reaction. Second, no signal is observed when the irradiation is turned on in the absence of the titrant. Both observations are valid for the entire range of experimental conditions. Third, observation shows that at this temperature (384 K) and the escape rate employed (aperture 3; Table I), the signal due to $m/e = 44$ increases and approaches a constant value immediately after starting the irradiation.

This behavior changes slightly at lower temperatures and smaller escape rates (i.e., higher pressures at comparable flow rates) as shown in Figure 4 (295 K, aperture 2; Table I). The isobutane- d_1 yield is somewhat larger than expected at short times after the irradiation starts and drops on a ~ 100 -s time scale to reach steady state. This behavior is more pronounced in the first experiments of a series and vanishes slowly with the number of experimental runs. Although the quantitative reproducibility of this effect is fairly poor (it varies on the time scale of days) and the database for this phenomenon is small, we attribute this observation to a heterogeneous reaction of the *tert*-butyl radicals with DBr (reaction 7), producing excess $i\text{-C}_4\text{H}_9\text{D}$ in the earliest stage of the experiment, after which the walls are "passivated". An effect like this might be expected to increase with increasing partial pressure of DBr and to decrease with increasing temperature of the walls. This is consistent with our observations. An additional observation is that the phenomenon is more pronounced in an experiment with a smaller DBr flow rate following an experimental run using a larger flow than in the case where the DBr flow is increased with the number of subsequent individual experimental runs ("memory effect"). This "overshoot" of the steady-state value is less important in the case of DI as a titrant. In the following data analysis, the steady-state level of the signals was used.

Neglecting reaction 7, the expression for the fractional yield, f , the ratio of the concentration of $i\text{-C}_4\text{H}_9\text{D}$ at a given titrant flow rate to its concentration at infinite titration (i.e., the initial radical concentration), has the form¹⁵

$$\frac{[i\text{-C}_4\text{H}_9\text{D}]_\infty}{[i\text{-C}_4\text{H}_9\text{D}]} = (1/f) = 1 + \frac{k_e^{\text{DX}}(k_e^{\text{R}} + k_w^I)V}{k_{1,2}F_{\text{DX}}^I}$$

where F_{DX}^I represents the flow rate of DBr or DI into the reactor in molecules s^{-1} , V is the reactor volume, k_e^{DX} and k_e^{R} are the escape rate constants of the titrant and the radical, respectively, k_w^I is the rate of the first-order wall loss of *tert*-butyl radicals, and $k_{1,2}$ is the homogeneous rate constant for reaction 1 or 2,

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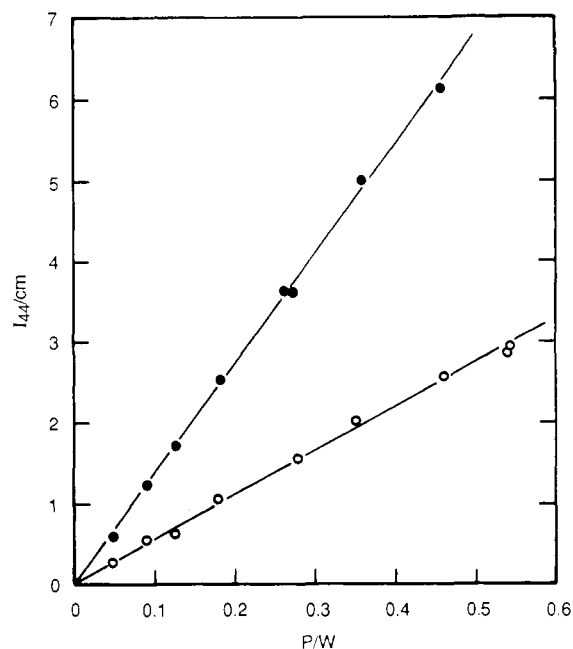


Figure 2. Mass spectrometric signal at $m/e = 44$ as a function of transmitted laser power. $F_{\text{AZO}}^I = 7.8 \times 10^{15} \text{ s}^{-1}$; $F_{\text{DBr}}^I = 5.54 \times 10^{15} \text{ s}^{-1}$. Aperture diameter: ●, 2 mm; ○, 3.2 mm.

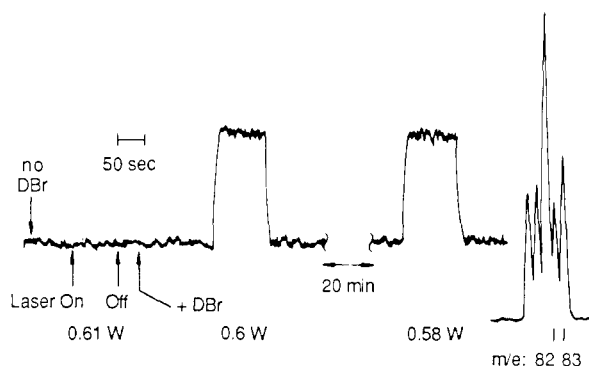


Figure 3. Mass spectrometric trace at $m/e = 44$ ($i\text{-C}_4\text{H}_9\text{D}$). Pulsed mode, 60 s^{-1} , 351 nm. $F_{\text{AZO}}^I = 9.9 \times 10^{15} \text{ s}^{-1}$, $F_{\text{DBr}}^I = 3.4 \times 10^{15} \text{ s}^{-1}$, 2-mm aperture, $T = 384 \text{ K}$. The mass spectrum on the right side represents the HBr/DBr ratio at this particular flow rate of DBr.

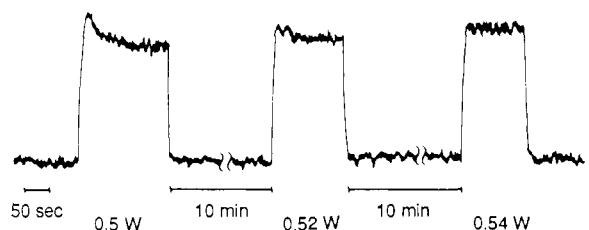


Figure 4. As in Figure 3, except with 1.5-mm aperture, $T = 295 \text{ K}$, $F_{\text{AZO}}^I = 7.0 \times 10^{15} \text{ s}^{-1}$, $F_{\text{DBr}}^I = 1.8 \times 10^{15} \text{ s}^{-1}$.

depending on whether DX is DI or DBr.

Thus, both $k_{1,2}$ and k_w^I can be determined from linear plots of f^{-1} versus $(F_{\text{DX}}^I)^{-1}$ for at least two different escape apertures. (This presupposes that k_w^I is a constant. In fact, it probably varies slightly with exposure of the walls to different doses of radicals and DX.) In order to compute the ordinate from measured values of the signal due to $i\text{-C}_4\text{H}_9\text{D}$, a value for this signal corresponding to total "titration" of the radicals is required. In principle, this is determined from the depletion of the azo compound. However, the azo compound depletion is only on the order of 1–2%, and this method would introduce substantial errors in the ordinate. Instead, we take advantage of the fact that, at the highest flow rates of DX employed, we are essentially at the total titration limit, that is, $\geq 95\%$ titration. This is easily ascertained by the fact that

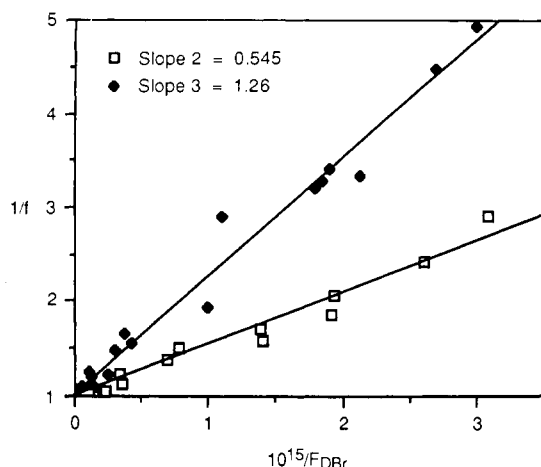


Figure 5. Inverse fractional yield of $t\text{-C}_4\text{H}_9\text{D}$ ($m/e = 44$) at 384 K versus inverse flow rate (in s/molecule) of DBr into the reactor. The symbols refer to the different escape rate constants (aperture sizes) given in Table I (\square , no. 2; \bullet , no. 3). F_{AZO}^i was between 5.0 and $9.0 \times 10^{15} \text{ s}^{-1}$ and constant for every individual experimental series. Every point represents a mean value of 2–6 single “laser-on-off-cycles”. The lines are based on a least-squares analysis but are forced through an intercept of 1.

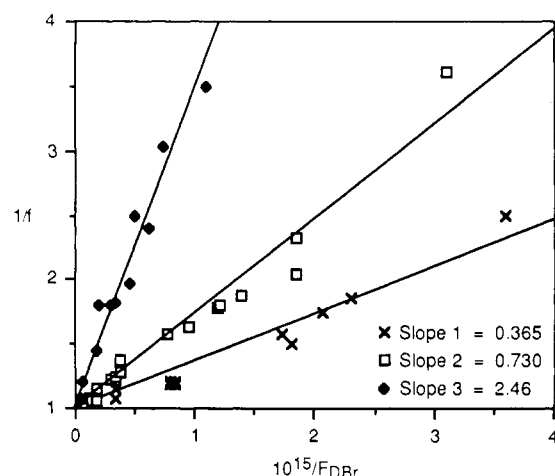


Figure 6. As in Figure 5 for $T = 295 \text{ K}$; $x =$ aperture 1 (Table I).

Table II. Measured Rate Constants for Reactions 1 and 2 $10^{-8}k$ ($\text{M}^{-1} \text{ s}^{-1}$)

aperture			T, K	DX	mean $k_{1,2}$
1	2	3			
0.52	1.27	0.91	295 ± 1.5	DBr	0.9 ± 0.4
	2.20	2.31	384 ± 6	DBr	2.3 ± 0.3
	3.0	1.2	295 ± 1.5	DI	2.1 ± 0.9
	3.1	1.0 ^a	384 ± 8	DI	3.1 ± 1.0

^a Windows not heated; data not used.

increases in the DX flow rate at this limit do not increase the signal.

Figure 5 shows the plot for the metathesis reaction of *tert*-butyl radicals with DBr at 384 K for two different escape rate constants (apertures 2 and 3 of Table I). Figure 6 shows the analogous plot at 298 K for three escape rate constants (apertures 1–3 of Table I). Figures 7 and 8 show similar results for *tert*-butyl reacting with DI. Table II presents a summary of individually determined experimental rate constants and a preferred, weighted mean value. All values are derived, setting $k_w^1 = 0 \text{ s}^{-1}$.

Variations in the rate constants determined assuming k_w^1 to be zero are within reasonable error. Those for k_1 are in good agreement with the Rossi and Golden³ values, and those for k_2 are consistent with expectations for the differences between DI and DBr. The values of k_2 are factors of 60 and 15 less than those of Russell et al. at 295 and 384 K, respectively! If heterogeneous second-order reactions are important, these differences are even

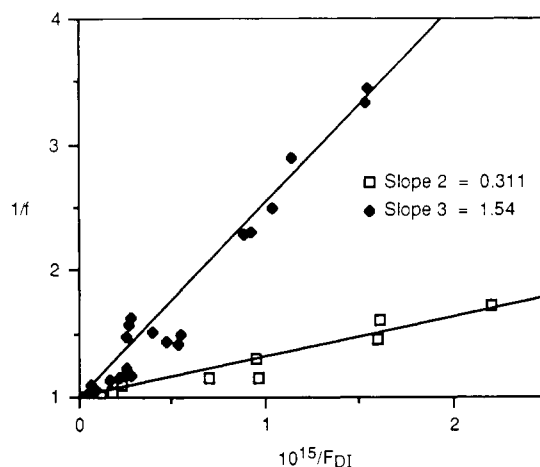


Figure 7. As in Figure 5 for the reaction of DI with *tert*-butyl radicals at $T = 384 \text{ K}$.

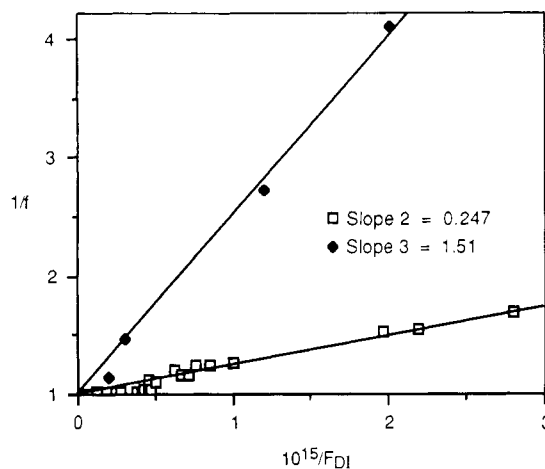


Figure 8. As in Figure 7, $T = 295 \text{ K}$.

larger, since our values are the sum of all second-order processes. If the data are used to calculate k_w^1 and $k_{1,2}$ directly from the equation as written, values of k_w^1 range between $+2$ and -1 s^{-1} , reflecting either small random errors or the aforementioned possibility of slight changes in surface character during the course of an experiment. In any case, k_w^1 is smaller than or of the same order as k_e^R . These small wall losses are in distinct contrast to those observed by Russell et al., whose values when translated from the surface area of their flow tube to that of our VLPΦ reactor would lead us to expect k_w (s^{-1}) as ~ 45 at 295 K and as 16 at 384 K!

In addition, as can be seen from comparison of Figures 5 and 6, or from the values of Table II, k_2 increases with increasing temperature. The effect is larger than the experimental uncertainty. This, of course, is inconsistent with the negative activation energy of -1.4 kcal/mol proposed by Russell et al.¹ for the analogous $\text{HBr} + t\text{-C}_4\text{H}_9$ reaction.

If there were a second-order heterogeneous reaction, such as reaction 7, one might anticipate a decrease in the relative importance of such a process at higher reactant pressure. This decrease is a result of the fact that the heterogeneous rate saturates at sufficiently high pressures. However, if saturation is not achieved, the heterogeneous rate will vary with pressure. The experiments in apertures 1–3 (Figure 6) correspond to the heterogeneous component of the rate being at, or near, saturation. We could then expect that an upper limit for the aperture size must exist beyond which the kinetics would be significantly influenced by heterogeneous contributions for the typical range of pressures used in this study.

Figure 9 shows experimental results at 384 K measured with an escape rate of a factor 2.5 larger than the largest escape rate used in the experiments shown in Figure 5 (aperture 4; Table I).

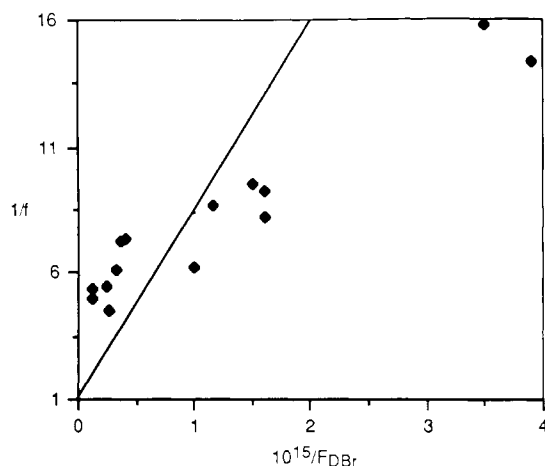


Figure 9. Inverse fractional yield of *i*-C₄H₉D at 384 K versus inverse DBr flow rate, measured with the largest aperture (no. 4; Table I; 3.2-mm diameter) in comparison with the expected line on the basis of the smaller escape rate experiments (—). $F_{\text{AZO}} = 7.5 \times 10^{15} \text{ s}^{-1}$.

For comparison, the expected line, calculated on the basis of the data presented in Figure 5, is also shown. The experimental points are evaluated according to the simple equation given above. However, with this larger aperture in place, we cannot achieve high enough flow rates of DBr to reach the total titration limit. The plot in Figure 9 was made by correcting the infinite titration value $[i\text{-C}_4\text{H}_9\text{D}]_{\infty}$ for the ratio of the escape rate constants k_{e} (aperture 4)/ k_{e} (aperture 3) (see Figure 1). Points taken at small flow rates (larger values of $(F_{\text{DBr}})^{-1}$) fall considerably under the expected straight line with unit intercept; this means too much isobutane-*d*₁ is produced to be attributed to the homogeneous reaction alone. The slope of the straight line through the experimental points displayed in Figure 9 would result in too small a value, thus to an erroneously large rate constant k_2 .

These experiments probably correspond to a situation where the heterogeneous component of the rate has not reached saturation. At the same time, a lower yield of isobutane-*d*₁ than expected is observed at high flow rates of the titrant. The reason for this behavior is not fully understood at present. The same sort of effects are seen in this aperture when DI is the titrating species. Thus, it would seem that an upper limit for the useful aperture size lies between apertures 4 and 3 (Table I) for the reactor used here. If the aperture is too large, there are problems of the type just discussed, namely, the increased importance of possible wall reactions, the difficulty in extrapolating to the total titration limit, and also the limited dynamic range of the $1/f$ measurement.

We conclude that the values for the rate constants given in the last column of Table II are essentially correct. After correction by $\sqrt{2}$ for the primary isotope effect, the values of k_2 are much smaller than derived from the studies of Russell et al. Our re-measured values of k_1 , shown in Figures 7 and 8 for 295 and 384 K and tabulated in Table II, agree with the rate constants given in ref 3 ($1.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 295 K and $3.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 384 K) within the limits given by the precision of the experiment.

The variation of approximately a factor of three observed for k_2 at 295 K may be simply random error, or it may come about as a result of changes in the rate of the heterogeneous component due to the changes in pressure during these experiments. Note that, at 384 K, where heterogeneous processes are expected to be less important, apertures 2 and 3 give exactly the same value for k_2 .

Some additional experimental findings are worthy of note. Preliminary experiments where *tert*-butyl iodide was employed as a radical precursor, instead of 2,2'-azoisobutane, and with the photolysis performed at 248 nm, yielded some evidence that secondary photolysis of the *t*-C₄H₉ free radical occurs at this wavelength. The amount of depletion of the precursor was much larger (up to 20%, monitored via the decrease of the $m/e = 57$ peak upon irradiation) than in the 2,2'-azoisobutane 351-nm experiment due to an increased absorption cross section at this

Table III. Thermochemical Data^f

	HBr	<i>t</i> -C ₄ H ₉	<i>i</i> -C ₄ H ₁₀	Br	Δ
S°_{298} , cal mol ⁻¹ K ⁻¹	47.44 ^a	74.81 ^c	70.42 ^b	41.80 ^a	-10.02
$\Delta H^\circ_{f,298}$, kcal mol ⁻¹	-8.66 ^a	9.2 ± 0.5^d	-32.15 ^b	26.74 ^a	-5.96
		9.9 ± 0.6^e			-6.65

^a Reference 16. ^b Reference 17. ^c References 13 and 14. ^d This work and ref 1. ^e This work and ref 6. ^f For the equation $\text{HBr} + t\text{-C}_4\text{H}_9 \rightarrow i\text{-C}_4\text{H}_{10} + \text{Br}$.

wavelength. There are two observations indicating that the situation is much more complex in the case of 248-nm photolysis: first, no recombination product (2,2,3,3-tetramethylbutane) could be observed at $m/e = 99$, whereas this was possible in the case of 351-nm photolysis of 2,2'-azoisobutane in the absence of any titrant; second, the mass spectrometric signal at $m/e = 57$ decreases in a distinctly nonlinear way as a function of the transmitted laser power. Even though the yields of *t*-C₄H₉ are 1 order of magnitude smaller upon 351-nm photolysis of 2,2'-azoisobutane, we preferred this situation to the more complex one for the case of the 248-nm irradiation of *i*-C₄H₉I where fast secondary photolysis processes seem to prevail.

Heat of Formation of *tert*-Butyl Radical. $\Delta H^\circ_{f,298}(t\text{-C}_4\text{H}_9)$ may be obtained on the basis of the present study of the metathesis reaction between DBr and *tert*-butyl radicals and the rate constant for the reverse reaction. There are two recent sources of rate parameters of the reverse reaction (referred to as -2 in the following). The first is a VLPR study⁷ where Br atoms were prepared by means of a microwave discharge through Br₂/He. This work yields

$$k_{-2} = 3.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$$

at 298 K. Some uncertainty in this study results from the fact that the discharge produces both excited atoms, Br* (²P_{1/2}), and ground-state Br (²P_{3/2}), which have different reactivities. The authors have applied a correction for this phenomenon. Rate constants larger by a factor of 3 are reported in the work of Russell et al. The expression given for the lower temperature range (298–478 K) of this study results in

$$k_{-2} = 9.13 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$$

at 298 K. The experiments were performed with a flash photolysis/bromine atom resonance fluorescence apparatus. The source of bromine atoms was the photolysis of CHBr₃ at $\lambda > 190 \text{ nm}$. The discrepancy between these two studies cannot be fully attributed to the uncertainties stated in each of them. The latter value comes from a much more extensive database and is in agreement with the values obtained at higher temperatures in the flow apparatus described earlier. We will report values for the heat of formation of *tert*-butyl radical based on both studies.

The entropy of *t*-C₄H₉ is well established. We use the calculated value of Pacansky and Yoshimine,¹⁴ which is $74.8 \pm 2.4 \text{ cal mol}^{-1} \text{ K}^{-1}$ at 298 K. This value is based on a calculated rotational barrier of 1.5 kcal mol⁻¹ for the CH₃ rotations and an assumed value of 200 cm⁻¹ for the pyramidal bending mode of the radical. This value is combined with the other thermochemical data listed in Table III in a third-law determination of the heat of formation. Our room-temperature value for k_2 (corrected by $\sqrt{2} \pm 0.35$ for the primary isotope effect) using $\Delta S^\circ_{R,298} = -10.02 \text{ cal mol}^{-1} \text{ K}^{-1}$ for reaction 2 yields $\Delta H^\circ_{R,298} = -5.96 \text{ kcal mol}^{-1}$, based on k_{-2} of Russell et al.¹ or $\Delta H^\circ_{R,298} = -6.65 \text{ kcal mol}^{-1}$ using k_{-2} from Kondo et al.⁷ These values yield $\Delta H^\circ_{f,298}(t\text{-C}_4\text{H}_9) = 9.2 \pm 0.5$ and $9.9 \pm 0.6 \text{ kcal mol}^{-1}$, respectively. The error limits reflect the uncertainty in $k_2(298)$ measured in this work, the accuracy of $S^\circ(t\text{-C}_4\text{H}_9)$, and the uncertainty in the exact value of the primary isotope effect correction factor.

These values for the heat of formation of the radical are in excellent agreement with the number given in the previous study of the more exothermic DI + *t*-C₄H₉ metathesis reaction by Rossi and Golden. The disparity with the high value of Russell et al.¹ ($\Delta H^\circ_{f,298} = 11.6 \text{ kcal mol}^{-1}$) is entirely caused by the high value

of k_2 and the negative activation energy that they report (-1.4 kcal mol $^{-1}$).

Summary

This investigation yielded rate constants for the metathesis reaction of *tert*-butyl radical with DBr at 295 and 384 K. After correction for the primary isotope effect, these are a factor of 50 or 11 smaller than obtained by Russell et al.¹ The reaction has a positive activation energy rather than the negative value reported in this same reference.

In combination with the measurements of the reverse reaction of Russell et al.,¹ one obtains

$$\Delta H_f^\circ_{298}(t\text{-C}_4\text{H}_9) = 9.2 \pm 0.5 \text{ kcal mol}^{-1}$$

in agreement with previous studies^{3,4} of the corresponding DI reaction that has also been remeasured in this study. No evidence for a complex mechanism involving a bound intermediate, as suggested in ref 1 has been found.

Special effort has been made to assess the possible interference of wall contributions and to find an appropriate range of experimental conditions.

Acknowledgment. W.M.-M. thanks the Deutsche Forschungsgemeinschaft for a fellowship and D.M.G.'s time was partially supported by DOE Basic Energy Sciences under Contract No. DE-FG03-86ER13571. Conversations with David Gutman have been friendly and stimulating.

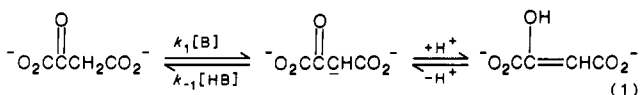
Catalysis of the Enolization of Oxaloacetic Acid by Primary and Secondary Amines via a Carbinolamine Intermediate

Paula Yurkanis Bruice

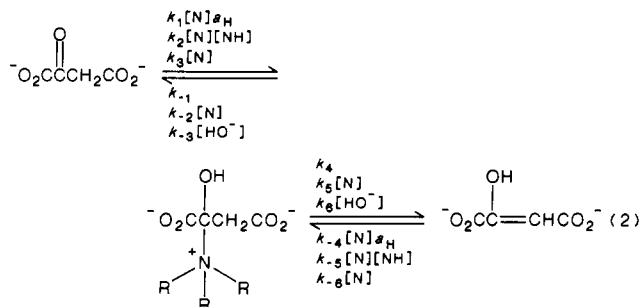
Contribution from the Department of Chemistry, University of California at Santa Barbara, Santa Barbara, California 93106. Received August 5, 1987

Abstract: The reaction of oxaloacetic acid has been investigated with six primary and six secondary amines. The amines were found to catalyze keto-enol interconversion in a rapid reaction prior to the formation of an imine or enamine. The enhanced reactivity of amines compared to oxyanions (relative second-order rate constants for a tertiary amine, secondary amine, primary amine, and oxyanion of $pK_a = 11$ are 915:264:100:1 for catalysis of oxaloacetate keto-enol interconversion, compared to 8.1:3.1:2.3:1 for proton abstraction from nitroethane) and the observation of a nonlinear dependence of rate on amine concentration suggests that amine-catalyzed keto-enol interconversion takes place via a carbinolamine intermediate rather than via the well-established simple proton-abstraction mechanism that occurs when the base catalyst is an oxyanion. This is the first example of primary and secondary amine catalyzed labilization of a keto α -hydrogen via a carbinolamine, a more rapid process than the well-known amine-catalyzed labilization of a keto α -hydrogen via imine formation.

We have previously shown that the enolization of oxaloacetic acid does not take place by the well-established base-catalyzed mechanism of eq 1 when the base employed is a tertiary amine.¹



The observations leading to this conclusion were the following: (1) the second-order rate constant for catalysis by a tertiary amine is as much as 2200 times greater than that for catalysis by an oxyanion of the same pK_a , a rate acceleration too great to be attributed to the enhanced ability of tertiary amines in removing a proton from carbon² and (2) enolization exhibits a nonlinear dependence of rate on amine concentration at low concentrations of tertiary amine. To account for these observations we proposed that oxaloacetic acid and tertiary amine react to form a carbinolamine intermediate which yields an enol on reaction with additional amine (eq 2).



The present paper describes our investigation of the kinetic behavior of primary and secondary amines with oxaloacetic acid. Although it is well-known that primary and secondary amines react with ketones to form imines and enamines, respectively,³ and that primary and secondary amines catalyze imine-enamine tautomerism,⁴ it has never been determined whether or not such amines are also capable of catalyzing keto-enol tautomerism. We have examined the reaction of oxaloacetic acid with six primary and six secondary amines and have found that the amines initially catalyze keto-enol interconversion in a mechanism similar to that proposed for tertiary amines, then subsequently form an imine or enamine.

Experimental Section

Materials. Oxaloacetic acid (Aldrich) was recrystallized twice from a 50/50 mixture of acetone and benzene. Anal. Calcd for $\text{C}_4\text{H}_4\text{O}_5$: C, 36.38; H, 3.05. Found: C, 36.19; H, 3.09. The amines employed were of the best available commercial grade and were used without further purification. All solids were dried in a vacuum desiccator over P_2O_5 .

Buffer Solutions. The amine-amine hydrochloride buffer solutions were prepared just prior to use by the addition of standardized 1.0 M

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