Wall Reactions in Acetone Photolysis

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The photolysis of acetone has been re-examined at temperatures between 107 and 225°C, and pressures between 0.13 and 133 mbar. In a Pyrex reaction vessel the wall reaction,

$$CH_3\cdot + (CH_3COCH_3)_{ads} \rightarrow CH_4 + CH_3COCH_2\cdot,$$

contributes significantly to methane formation at acetone pressures below 10 mbar. The rate of this reaction is proportional to the methyl radical concentration in the gas phase, and varies markedly with the nature of the surface. On PTFE and PbO surfaces the rate of reaction appears independent of acetone pressure in the range 0.13-2.7 mbar, but on Pyrex it increases slowly with increasing acetone pressure. On Pyrex surfaces the reaction has an activation energy of 6.6±1.0 kcal mol^{-1} and is always faster on a *per collision* basis than the analogous reaction in the gas phase.

The photolysis of acetone with 313 nm light at temperatures above 100°C involves the following homogeneous processes,[1, 2]

$$CH_3COCH_3 \xrightarrow{h\nu} CH_3\cdot + CH_3CO\cdot \tag{1}$$

$$CH_3CO\cdot(+M) \rightarrow CH_3\cdot + CO(+M) \tag{2}$$

$$CH_3\cdot + CH_3COCH_3 \rightarrow CH_4 + \dot{C}H_2COCH_3 \tag{3}$$

$$CH_3\cdot + CH_3\cdot \rightarrow C_2H_6 \tag{4}$$

$$CH_3\cdot + \dot{C}H_2COCH_3 \rightarrow C_2H_5COCH_3 \tag{5}$$

$$2\dot{C}H_2COCH_3 \rightarrow (CH_3COCH_2)_2. \tag{6}$$

Under these conditions, (2) is sufficiently fast for alternative reactions of acetyl to be negligible,[3] although at lower temperatures and high intensities,

$$CH_3CO\cdot + CH_3\cdot \rightarrow CH_4 + CH_2CO \tag{7}$$

makes important contributions to the yield of methane.[4] Acetone photolysis has consequently been much used as a source of methyl radicals for the measurement of the kinetic parameters for their hydrogen-abstraction reactions by comparison with those of reaction (4).[5] The most reliable measurement of the rate constant of reaction (4) involved the application [6] of the rotating sector method to acetone photolysis at 165°C.

In studies of acetone photolysis at temperatures in the region of 250°C, Dodd and Steacie,[7] and Kistiakowsky and Roberts,[6] have assumed that reactions (3) and (4) are the only ones which form methane and ethane, so that,

$$\rho \equiv v(C_2H_6)[CH_3COCH_3]^2/v^2(CH_4) = k_4/k_3^2, \tag{i}$$

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where $v(C_2H_6)$ and $v(CH_4)$ are the observed rates of formation of ethane and methane The pressure-dependence of ρ, which becomes marked below 15 mbar, was then attributed to the third-body requirements of reaction (4).

There are indications that this interpretation is over-simplified : Dodd and Steacie themselves observed that an increase in the surface/volume ratio of their vessel had the same effect on the product distribution as the postulated pressure-dependence of k_4. Shaw and Toby,[8] finding positive intercepts on the ϕ axis for plots of

$$\phi \equiv v(CH_4)/\sqrt{v(C_2H_6)} \qquad \text{(ii)}$$

against acetone pressure, suggested that at low pressures a molecular elimination of methane occurred,

$$CH_3COCH_3^* \rightarrow CH_4 + CH_2CO,$$

from vibrationally excited acetone in the ground electronic state. The ϕ intercepts they measured from their own results and from those of Dodd and Steacie appeared to vary with the surface/volume ratio of the vessel, but Shaw and Toby believed that the variations were not significant. In comparing the photolysis of acetone and acetone+azomethane mixtures, Ausloos and Steacie [4] noted, for both systems, a curvature at low temperatures of the Arrhenius plots for the experimental quantities which on the mechanism of reactions (1)-(6) correspond to $k_3/\sqrt{k_4}$. No such curvature was found for the photolysis of azomethane alone, and Ausloos and Steacie concluded that at low temperatures a wall reaction between methyl and adsorbed acetone must supplement methane formation by (4).

The experiments described here were undertaken as part of a study of the diffusion of methyl radicals; they provide direct evidence of a dark reaction at the wall in which methane is formed from methyl radicals, thereby confirming the hypothesis of Ausloos and Steacie.

EXPERIMENTAL

Reaction rates were measured by analyzing by gas chromatography the products formed during measured periods of illumination. The light source was the compact Osram HBO 100 W super-pressure mercury lamp, and its unfiltered output was accurately collimated by a quartz lens and three stops. The lamp was operated on a 110 V d.c. battery supply adjusted to give constant intensity as indicated by a device based on the R.C.A.935 phototube. No lamp was used for more than 100 h and during this period the power fluctuation was less than 2 %. The neutral density filters were prepared by evaporating on to a quartz plate a thin film of Inconel; they had an almost perfectly neutral transmission characteristic in the range 240-350 nm.

The cylindrical quartz reaction vessel shown in fig. 1 was designed to give ease of access to the working space. The end of the vessel nearer to the light source was an optical quartz plate; the other end was closed by a removable evacuated cell which provided the necessary thermal insulation and also had optical quartz plate ends. For the experiments described here the 29.8 cm long working space of the cell contained a Pyrex reaction sleeve which was coaxial with it and 1 mm shorter. The light beam was also carefully aligned to be coaxial with the sleeve, and its diameter was adjusted so that it filled the interior of the sleeve exactly. Sleeves of 6.7, 9 and 18 mm int. diam. were used; they were cleaned by being washed successively in organic solvent, chromic acid and 4 % hydrofluoric acid. Lead oxide (PbO) surfaces were prepared by evaporating a film of lead on to the interior surface of a sleeve, and then oxidizing this film at 350°C in a stream of oxygen dried over silica gel. Polytetrafluoroethylene (PTFE) surfaces were prepared by wetting the interior of a Pyrex sleeve with a diluted Dupont 852-201 Teflon emulsion, and allowing the surface to dry, after which the PTFE film was " cured " by warming the sleeve in a cool Bunsen flame until it was transparent. The reaction vessel fitted closely into a triply wound electrically heated aluminium block furnace which was controlled electronically. The temperature of the working section of the cell was constant in time to ±0.1°C and in space to ±0.5°C.

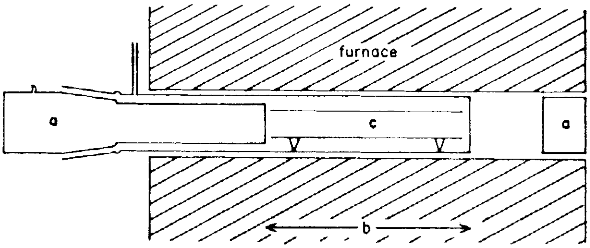

FIG. 1.—Schematic diagram of the reaction vessel; *a*, evacuated transparent thermal insulating cells; *b*, working space of the reaction vessel; *c*, reaction sleeve.

The vacuum equipment was of conventional design and construction, but those taps that came into contact with acetone vapour were of the greaseless Springham type with neoprene diaphragms. After each run the reaction products were expanded into a Töpler pump from which, after compression, samples were withdrawn and injected into the chromatograph by means of a specially designed valve. The chromatograph used a catharometer and a flame ionization detector in series, with hydrogen as the carrier gas. The analyses were performed at 59°C on a 2.88 m column of 100-120 mesh alumina treated with 5 % by weight of NaOH.

The reactant was Eastman-Kodak Spectro-grade acetone which was dried over anhydrous calcium sulphate and subjected to a repeated trap-to-trap distillation with the rejection of large head and tail fractions. It was stored in an opaque trap and bulb. The carbon dioxide was the grade X supplied by B.O.C. and was used without further treatment. Phillips Research-grade methane and ethane were used in calibrating the chromatograph.

RESULTS

The first set of experiments relate to the variation of ρ with acetone pressure. Acetone was photolyzed at pressures between 0.13 and 80 mbar (0.1 and 60 torr) at 127°C with an effective vessel diameter of 18 mm, and a light beam of constant intensity which completely filled this space. The results are present in fig. 2; they show that while the variation of ρ with pressure is qualitatively of the form required by unimolecular reaction theory, the slope of the curve at low pressures is close to 2.5 whereas the maximum permitted by theory is unity. We conclude that, while the pressure-dependence of k_4 may contribute to the variation of ρ with acetone pressure, this effect alone is incapable of accounting for our observations. The divergence between the experimental results and the predictions of the mechanism of Dodd and Steacie can be accounted for by postulating that methane production by reaction (3) is supplemented by another reaction at low acetone pressures.

To study the kinetics of this supplementary source of methane we have carried out experiments under conditions for which k_4 is expected to be constant and close to its infinite pressure value. Acetone at partial pressures of 0.13-2.67 mbar was photolyzed in the presence of sufficient carbon dioxide to give a total pressure of 40 mbar. The experiments were again carried out at 127°C with an 18 mm diam. sleeve. Three sets of runs were carried out; in the first, the inner surface of the clean Pyrex reaction sleeve was untreated; in the second, it was coated with a thin film of PTFE, and in the third with a layer of PbO. The results are presented in fig. 3

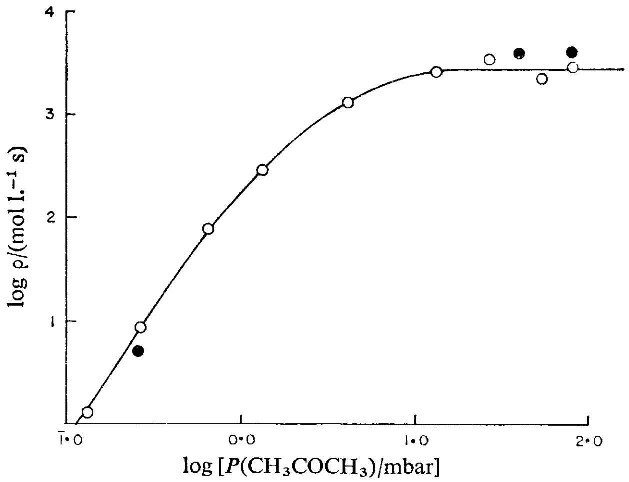

FIG. 2.—Variation of ρ with acetone pressure at 127°C. ○, series 1 ; ●, series II.

as plots of ϕ against acetone pressure $P(CH_3COCH_3)$. Also shown in fig. 3, as a broken line is the quantity

$$\phi = P(CH_3COCH_3)\phi_{133}/133, \qquad \text{(iii)}$$

where ϕ_{133} is the value of ϕ measured for the photolysis of 133 mbar of acetone alone under identical conditions of vessel geometry and temperature. This line represents our estimate of the expected homogeneous contribution to ϕ at low partial pressures of acetone.

The results show unequivocally that the supplementary methane source is a heterogeneous reaction. Since the lines for the PbO and PTFE surfaces are parallel to that of eqn. (iii), the rate of the heterogeneous reaction must be independent of acetone pressure on these surfaces. On Pyrex, however, the line is of slightly greater slope, implying that on this surface the rate of the wall reaction increases with acetone pressure, possible by virtue of increased surface coverage by acetone.

In blank experiments under similar conditions but in the absence of illumination,

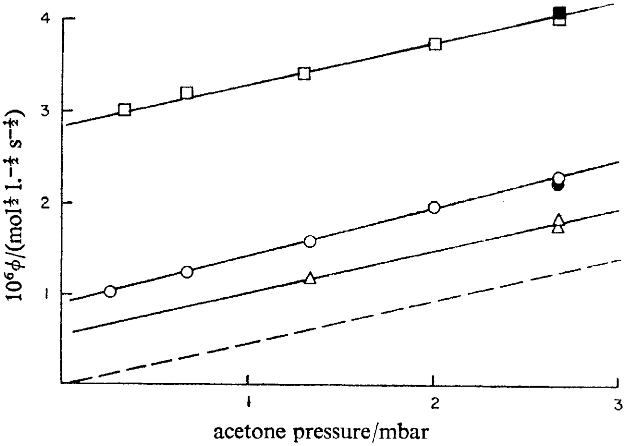

FIG. 3.—Variation of ϕ with acetone partial pressure at 127°C with CO_2 added to give a total pressure of 40 mbar. ○, Pyrex surface; △, PTFE, surface: □, PbO surface. Filled points correspond to 1/20 normal intensity. The broken line corresponds to equation (iii).

no methane or ethane was formed. The use of a neutral density filter to reduce the light intensity to 1/20 of its original value had no significant effect on the value of ϕ for experiments with PbO and Pyrex surfaces. The results of these experiments are shown as filled points on fig. 3. Clearly the rate of the heterogeneous methane source shows the same dependence on light intensity as that of the homogeneous source, which varies as the square root of the intensity. The only explanation for these observations is that methyl radicals release methane at the wall by reaction with adsorbed acetone molecules.

Support for this conclusion derives from a study of the dependence of ϕ on surface/volume ratio. Fig. 4 includes the results of experiments, similar to those the results of which are given in fig. 3, Pyrex reaction sleeves of diameter 9 and 6.7 mm being used. In each case the light exactly filled the space enclosed by the sleeve, and the

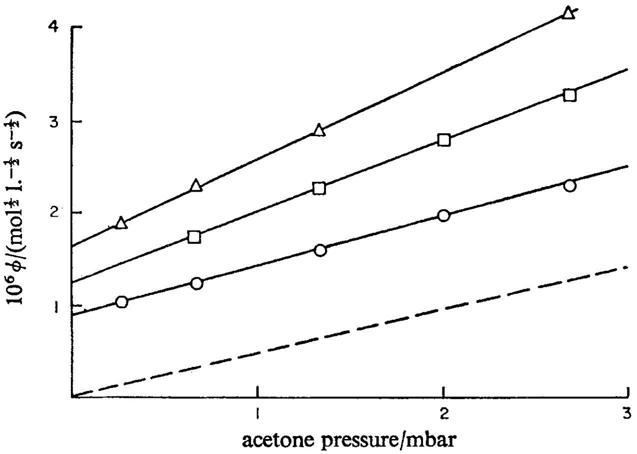

FIG. 4.—Variation of ϕ with acetone partial pressure at 127°C and a total pressure of 40 mbar. ○, $S/V = 2.29\ \text{cm}^{-1}$; □, $S/V = 4.51\ \text{cm}^{-1}$; △, $S/V = 6.04\ \text{cm}^{-1}$. The broken line corresponds to eqn (iii).

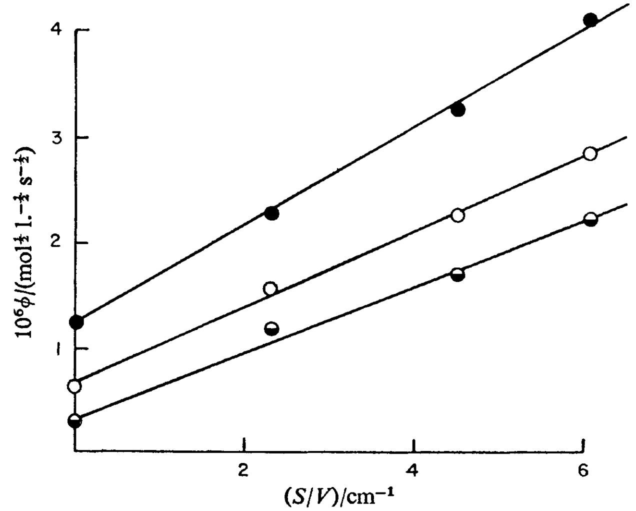

FIG. 5.—Variation of ϕ with S/V at 127°C and 40 mbar total pressure. ●, 2.67 mbar CH_3COCH_3; ○, 1.33 mbar CH_3COCH_3; ⊖, 0.67 mbar CH_3COCH_3. All reaction sleeves of Pyrex.

acetone was diluted with carbon dioxide to a total pressure of 40 mbar. Some of these results are replotted in fig. 5 to show the variation with surface/volume ratio of the value of ϕ at fixed acetone pressures. The values for surface/volume ratio = 0 are derived from eqn. (iii). The plots of fig. 4 and 5 confirm that on Pyrex surfaces the rate of the heterogeneous reaction is indeed a function of acetone pressure and is proportional to the surface/volume ratio.

Finally, we have examined the temperature-dependence of the heterogeneous methane source. Our experiments involved the photolysis of acetone at temperatures in the range 107-225°C in an 18 mm Pyrex reaction sleeve. All the experiments used 1.33 mbar of acetone diluted in carbon dioxide to a total pressure of 40 mbar. Using eqn (iii) to calculate the homogeneous contributions to our observed values, ϕ_{obs}, we estimate the heterogeneous contribution as,

$$\phi_{\text{het}} = \phi_{\text{obs}} - (\phi_{133}/100).$$

The results are presented in fig. 6 as an Arrhenius plot from which the activation energy of the heterogeneous process is derived as 6.6 ± 0.8 kcal mol^{-1}.

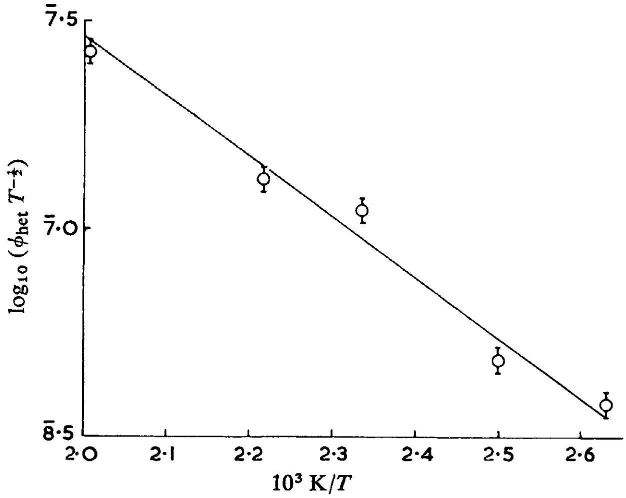

FIG. 6.—Arrhenius plot for ϕ_{het} at 1.33 mbar of acetone and a total pressure of 40 mbar for 18 mm diam. Pyrex sleeve; $E_a = 6.63$ kcal mol^{-1}.

DISCUSSION

All these results may be accounted for by adding to the mechanism (1)-(6) the surface reaction

$$CH_3\cdot + (CH_3COCH_3)_{\text{ads}} \rightarrow CH_4 + (CH_3COCH_2\cdot)_{\text{ads}} \tag{8}$$

proposed by Ausloos and Steacie. Our finding that ϕ is independent of the incident intensity when the surface process is important is incompatible with the concept of a direct photolysis of adsorbed acetone.[10]

The rate v_8 of the supplementary source of methane we write as

$$v_8 = k_8(S/V)[CH_3\cdot]_{\text{wall}},$$

where S/V is the surface/volume ratio of the vessel, and $[CH_3\cdot]_{\text{wall}}$ is the gas-phase concentration of methyl radicals near to the wall. It then follows that, in general,,

$$\phi = \frac{k_8}{\sqrt{k_4}}\frac{S}{V}\frac{[CH_3\cdot]_{\text{wall}}}{\sqrt{[CH_3\cdot]^2}} + \frac{k_3}{\sqrt{k_4}}\frac{\overline{[CH_3\cdot]}}{\sqrt{[CH_3\cdot]^2}}[CH_3COCH_3], \tag{iv}$$

where $\overline{[CH_3\cdot]}$ and $\overline{[CH_3\cdot]^2}$ are the mean and mean square concentrations of radicals in the reaction volume. If the wall reaction is diffusion-controlled,

$$[CH_3\cdot]_{\text{wall}} \ll \overline{[CH_3\cdot]} \neq \sqrt{\overline{[CH_3\cdot]^2}}.$$

In the region of kinetic control, however, all three of these concentrations are equal, so that,

$$\phi = \frac{k_8 S}{\sqrt{k_4}V} + \frac{k_3}{\sqrt{k_4}}[CH_3COCH_3]. \tag{iv$'$}$$

We now assume kinetic control at the wall, and justify our assumption *a posteriori.*

For PTFE and PbO surfaces the lines of fig. 3 are parallel to the line corresponding to the homogeneous contribution to ϕ. The intercepts of these lines may therefore be identified with $(k_8/\sqrt{k_4})$ (S/V) and allow a determination of k_8 by comparison with the value [6, 9, 11] of $k_4 = 2.2 \times 10^{10}$ mol^{-1} l. s^{-1}. For the Pyrex surfaces k_8 is a function of acetone pressure, and has been calculated for 1.33 mbar of acetone by subtracting from our observation of ϕ the homogeneous contribution calculated from eqn. (iii). When values for k_8 were calculated, allowance for reaction on the quartz windows was made by assuming their reactivity to be equal to that of Pyrex. The results are presented in table 1, the final column of which shows k_8 expressed as an efficiency γ per wall collision.

TABLE 1.—WALL REACTION VELOCITY CONSTANTS AT 127°C

surface	S/V (cm^{-1})	k_8 (cm s^{-1})	γ
Pyrex	2.29	0.060*	3.2×10^{-6}
Pyrex	4.51	0.054*	2.9×10^{-6}
Pyrex	6.04	0.056*	3.0×10^{-6}
PTFE	2.29	0·036	1.9×10^{-6}
PbO	2.29	0.190	1.0×10^{-5}

* A function of acetone pressure: values shown for 1.33 mbar of acetone.

An approximate criterion for the transition from kinetic control to diffusion control may be derived as follows. When reactions involving $\dot{C}H_2COCH_3$ are neglected, the mass balance equation for methyl radicals in the steady state is

$$D\nabla^2 c + R_i - 2k_4 c^2 = 0, \tag{v}$$

where D is the diffusion coefficient for methyl radicals, c their local concentration and R_i the rate of photo-initiation. At the wall, the boundary condition is

$$-D(\mathrm{d}c/\mathrm{d}r)_{\text{wall}} = k_8 c_{\text{wall}}. \tag{vi}$$

Solving eqn. (v) for long cylindrical geometry by the linear approximation method outlined by Marshall and Quinn [12] for spherical geometry, we find that when the concentration gradients are small,

$$\bar{g}/(1-\bar{g}^2) = A(B+4)/8B,$$

where $g = c/c_0$, $A = 2k_4 c_0 a^2/D$, $B = ak_8/D$, $c_0 = \sqrt{(R_i/2k_4)}$, and a is the radius of the vessel. From the form of this solution we deduce that diffusion control sets in when $k_8 > 4D/a$. Using a collision diameter of 0.38 nm for $CH_3\cdot + CO_2$ we estimate that at 127°C and 40 mbar, $D = 8.8$ cm^2 sec^{-1}, so that for a 1.8 cm diam. vessel, diffusion control of the surface reaction would only set in for $k_8 > 40$ cm/sec, i.e., for wall efficiencies in excess of 2×10^{-3}. As the values derived here are at least two orders of magnitude smaller, the wall reaction must be kinetic controlled under our experimental conditions.

If the acetonyl radical formed in reaction (8) reacts before it is desorbed, reaction (8) constitutes a wall-termination process. We have therefore compared our results with those obtained for other systems. For hydrogen atoms on acid-washed silica, Green *et al.*[13] found efficiencies about 20 times greater than those of the present work, and for oxygen atoms, Greaves and Linnett [14] found a wall efficiency for HF-washed Pyrex of 3×10^{-5} at room temperature. PbO surfaces are much more reactive than Pyrex for the removal of both oxygen and hydrogen atoms.[14, 15] and PbO is an effective inhibiting surface for ethane pyrolysis.[16] PTFE coating is now commonly used to " poison " flow tubes for experiments with hydrogen, oxygen and nitrogen atoms, but while we find PTFE to be less reactive than Pyrex in our system, its efficiency is only about 30 % lower. Thus, while the order of reactivity of the three surfaces used here is the same as that found for other systems, the absolute values of the reactivities are smaller for methyl, and the range of reactivities for the three surfaces is probably smaller. Our results suggest that the PTFE " poisoning " of flow tubes may well be less efficient in the presence of organic reactants.

The activation energy we have measured for k_8 on Pyrex corresponds at 127°C to a collision efficiency of $2{\cdot}4 \times 10^{-4}$. Our observed value of γ at this temperature was 3.2×10^{-6}, suggesting a " steric factor " of 1.3×10^{-2}. For the corresponding process in the gas phase, reaction (3), the activation energy and " steric factor " are [17] 9.7 kcal mol^{-1} and 1.8×10^{-3}, corresponding to a collision efficiency of about 10^{-8} at 127°C. On a *per collision* basis the wall process is thus always faster than the corresponding gas-phase reaction.

There is no reason to expect the reaction (3), of methyl with acetone to be unusual in having a heterogeneous analogue, reaction (8), which takes place with comparable or greater collision efficiency. If such analogues exist generally, due allowance should be made in any radical reaction system with reactant pressures less than about 10 mbar in vessels of normal geometry. The authors know of no occasion on which such an allowance has been made.

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