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(9) In most of the chromophore–quencher complexes examined earlier (e.g., those linked by covalent methylene spacer units[10-12]), the absorption spectrum of the supramolecule is simply the sum of the chromophore and quencher fragments. This is not the case with the present Ru–dpp–Rh complex. As elaborated later in the results and discussion section, the CT absorption of the Ru(II)-based chromophore is red-shifted with respect to the parent mononuclear complex. (Even in the homobinuclear complex $[(bpy)_2Ru\text{–}dpp\text{–}Ru(bpy)_2]^{4+}$, the same question on the existence of discrete/independent chromophoric units can be raised.) Arguments have been advanced that ground-state absorption spectral shifts by themselves are not true indicators of the extent of interaction between the two metal centers.

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Electron Transfer from $CO_2^{\bullet -}$ to Perylene in Cyclohexane[1]

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$CO_2^{\bullet -}$ formed by the reaction of the electron with CO_2 in cyclohexane transfers an electron to perylene with a rate constant of 2.9×10^{10} M^{-1} s^{-1}. $G\epsilon_{580nm}$ for the perylene radical anion is 9×10^3 molecules (100 eV)$^{-1}$ M^{-1} cm^{-1}. The transfer of an electron from $CO_2^{\bullet -}$ to an aromatic molecule is a significant process when CO_2 is used as an electron scavenger in solutions where the production of excited states of the aromatic molecule is studied.

Introduction

To determine mechanisms in hydrocarbon radiolysis, scavengers have frequently been used to separate the various chemical processes that can occur. In particular, electron scavengers are often used to retard ion recombination, which is very rapid with the highly mobile electron. The ideal electron scavenger creates species whose reactions are both well defined and slower than the reactions of the electron. Carbon dioxide is often used as an electron scavenger in radiolysis studies in nonpolar solvents. The equilibrium $e^- + CO_2 \rightleftharpoons CO_2^{\bullet -}$ has been investigated,[2,3] and for CO_2-saturated solutions the ratio of $CO_2^{\bullet -}$ to e^- is greater than 10^6. In cyclohexane CO_2 reacts with the electron at a rate constant[4] of 4.3×10^{12} M^{-1} s^{-1}. The resulting $CO_2^{\bullet -}$ is an electron-rich molecule, and it is important to know whether it can transfer an electron to solutes such as aromatic molecules if one is to make use of CO_2 as a reactant to modify the ionic processes in geminate recombination in a known way. In nonpolar solvents a few results have been reported on electron transfer reactions of $CO_2^{\bullet -}$; it was found to live long enough (ca. 10^{-5} s) to react with the galvinoxyl radical,[5] and the rate constants for electron transfer to O_2 have been determined to be 1.3×10^9 M^{-1} s^{-1} in 2,2,4-trimethylpentane and 1.4×10^{10} M^{-1} s^{-1} in tetramethylsilane.[6] In aqueous solution, there have been a greater number of studies of $CO_2^{\bullet -}$ reactions. Frank et al. have concluded that the radical anion of pyrene transfers an electron to CO_2, and $CO_2^{\bullet -}$ transfers an electron to the triplet state of pyrene.[7] A series of studies on reactions of $CO_2^{\bullet -}$ with ruthenium complexes has been reported by Hoffman and co-workers,[8-12] and rate constants in the range of 2.5×10^9 to 1.3×10^{10} have been determined.[8] Other studies of $CO_2^{\bullet -}$ in aqueous solution have also been reported; a nonexhaustive list is given in refs 13–16. Here, we report on the transfer from $CO_2^{\bullet -}$ to perylene in cyclohexane solution.

Experimental Section

Pulses of 20-MeV electrons were obtained from the Argonne National Laboratory (Chemistry Division) linear accelerator. The pulse duration used was 4 ns (fwhm), and doses per pulse ranged from 2 to 8 krad. Dosimetry was performed by measuring the

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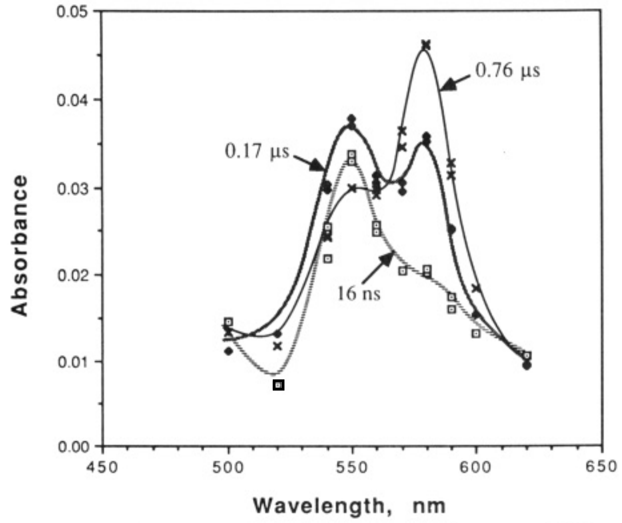

Figure 1. Transient spectra in cyclohexane containing 5 × 10^{-5} M perylene and 0.066 M CO_2 irradiated with an 8.1-krad pulse; absorbance per 2 cm path length. Wavelength discrimination was obtained with interference filters (9–10 nm bandpass); the maxima are for filters of 550 and 580 nm.

optical absorption of the solvated electron in water at 500 nm, where its molar absorptivity has been determined to be[17] 5.4 × 10^3; a G value at the end of the 4-ns pulse of 3.7 solvated electrons per 100 eV absorbed was used.[18]

Samples were irradiated in cells with Suprasil windows, having an optical path length of 2 cm, with the analyzing light beam passing through the cell in a direction opposite to that of the electron beam.

The sample cells were filled from syringes of the solutions which were purged of air and saturated with CO_2 by repeated shaking and expulsion of the gas. These techniques have been described in detail previously.[19] The cyclohexane was Burdick and Jackson "distilled in glass" grade which was passed through a column of silica gel which had been baked at 300 °C. The perylene was Aldrich Gold Label Grade, 99+%, and was used as received.

The system for measurement of transient absorptivity consisted of a 75-W Xe lamp which was pulsed during the observation period, an optical system to transport the light to an interference filter (9–10 nm bandwidth) at the desired wavelength, a photodiode (CD-10) as a detector, and a Tektronix 7912 digitizer. Data from the digitizer were averaged in a computer.

Results and Discussion

The radical cation and anion of perylene have absorption maxima at 535 nm (concentrated sulfuric acid solution, $\epsilon = 4.8 \times 10^4$ M^{-1} cm^{-1}) and 572 nm (1,2-dimethoxyethane with Li, $\epsilon = 5.0 \times 10^4$ M^{-1} cm^{-1}), respectively.[20] Spectra are also reported in Shida's compilation; the cation has a maximum at 543 nm in a Freon matrix, with no value for the molar absorptivity reported, and the anion has a maximum at 578 nm in a MTHF (methyltetrahydrofuran) matrix with $\epsilon = 5.7 \times 10^4$ M^{-1} cm^{-1}.[21] The absorption spectrum of the radical anion has also been determined by an electron photodetachment method;[22] absorption maxima in the range of 575–580 nm were obtained in tetramethylsilane, 2,2,4-trimethylpentane, and n-pentane. Spectra obtained in the 500 to 600 nm region are given in Figure 1 for a CO_2-saturated cyclohexane solution containing 5 × 10^{-5} M perylene (Pe). The absorbance at 580 nm, ascribed to $Pe^{\bullet-}$, takes approximately a microsecond to reach a maximum; the absorbance at 550 nm, ascribed to $Pe^{\bullet+}$, grows in much more rapidly and begins to decay while the $Pe^{\bullet-}$ is still forming. The kinetics, measured at 550 and 580 nm, are shown in Figure 2.

The formation of $Pe^{\bullet-}$ is ascribed to the following reactions:

$$e^- + CO_2 \Rightarrow CO_2^{\bullet-} \qquad (1)$$

$$CO_2^{\bullet-} + Pe \Rightarrow Pe^{\bullet-} + CO_2 \qquad (2)$$

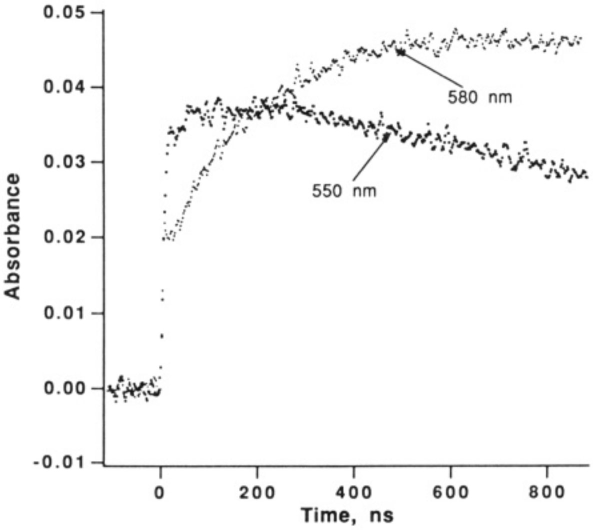

Figure 2. Absorbance vs time at 550 and 580 nm in cyclohexane containing 5 × 10^{-5} M perylene and 0.066 M CO_2 irradiated with an 8.1-krad pulse (absorbance per 2 cm path length).

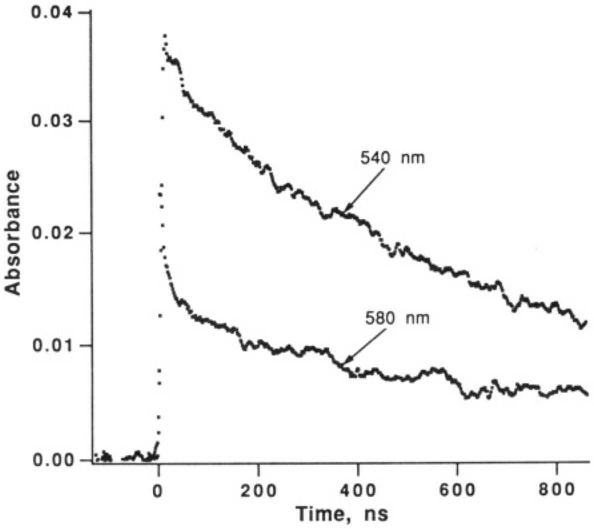

Figure 3. Absorbance vs time at 540 and 580 nm in cyclohexane containing 5 × 10^{-5} M perylene and 0.12 M N_2O irradiated with an 11-krad pulse (absorbance per 2 cm path length).

This assignment is based on both kinetic and yield data that will be discussed below. The reaction clearly involves the CO_2 molecule because in the absence of the CO_2 there is no comparable growth. Also the reaction of the electron with the perylene is not the dominant reaction because in the presence of CO_2 the formation of the 580-nm absorbance would be expected to be much faster. The reaction leading to the 580-nm absorbance is not simply due to the presence of an electron scavenger because no similar growth is seen in the presence of N_2O (see Figure 3) or CCl_4. Once the electron is captured by these molecules, it apparently cannot be transferred to Pe. This may be due to fragmentation of the molecule following electron capture and unfavorable energetics involving transfer from the fragment negative ion. Note however that there is evidence that $N_2O^{\bullet-}$ in cyclohexane does not rapidly fragment.

The rate constant of reaction 2 was determined by measuring the formation of the 580-nm absorbance as a function of [Pe]. The pseudo-first-order rate constant for the formation was determined at each [Pe] using a nonlinear least-squares fitting method, assuming a first-order formation followed by a second-order decay. The experimental formation curves showed that part of the absorbance was formed essentially instantly, so an initial absorbance was included in the fitting parameters. An example of the fit to the experimental data is shown in Figure 4. In Figure 4a data from 0 to 43 μs were used to determine the second-order

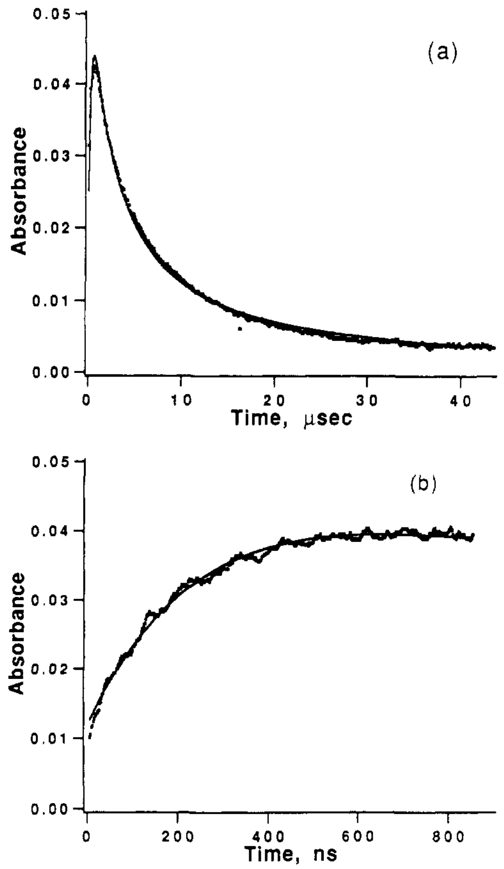

Figure 4. Absorbance vs time at 580 nm in cyclohexane containing 1 × 10^{-4} M perylene and 0.066 M CO_2 irradiated with a 2.5-krad pulse (absorbance per 2 cm path length). The dots represent experimental data and the lines are from the fitting procedure.

decay constant, which was used as a fixed parameter in part b, a shorter time scale, to determine the formation constant.

The results in Figure 4a show that the decay of the absorption due to $Pe^{\bullet -}$ is second order, which is expected if homogeneous, second-order ion recombination is the decay mechanism. The formation kinetics (Figure 4b) are well fit by pseudo-first-order kinetics, as expected for reaction 2.

If the $CO_2^{\bullet -}$ were entirely from scavenging of free electrons, analysis of the formation constants, k_{obs}, obtained from the fitting procedure, to obtain k_2 would be straightforward as described by eq I

$$k_{obs} = k_0 + k_2[Pe] \qquad (I)$$

where k_0 represents pathways other than transfer of an electron to Pe for disappearance of $CO_2^{\bullet -}$. Two other reaction pathways will affect the formation and decay of $CO_2^{\bullet -}$. First, $CO_2^{\bullet -}$ free ions can react with positive ions to some extent during the formation period, and this is a second-order reaction, so its inclusion in the term k_0 is an approximation. (That this is a significant process is indicated by the fact that the observed yield of $Pe^{\bullet -}$ absorption decreased significantly when the dose per pulse was increased.) Second, some of the $CO_2^{\bullet -}$ is geminate and decays by geminate recombination, which does not have first-order kinetics, so including it in k_0 is also an approximation. An additional problem is that $Pe^{\bullet -}$ formed by transfer from geminate $CO_2^{\bullet -}$ also decays geminately, which will have a small effect on the derivation of k_0 in the fitting process. Because these pathways are not quantitatively treated, eq I will hold only over a limited [Pe] range.

A plot of the formation constants, k_{obs}, vs [Pe] is shown in Figure 5. There is no evidence that the approximations discussed above cause any problems, but with the experimental scatter, a small deviation from linearity would be difficult to discern. The slope of this plot is 2.9 × 10^{10} M^{-1} s^{-1}, which is the rate constant k_2. This value is approximately that expected for a diffusion limited reaction of $CO_2^{\bullet -}$. The intercept is k_0 = 5 × 10^5 s^{-1}, which corresponds to all paths for disappearance of $CO_2^{\bullet -}$ other than reaction 2.

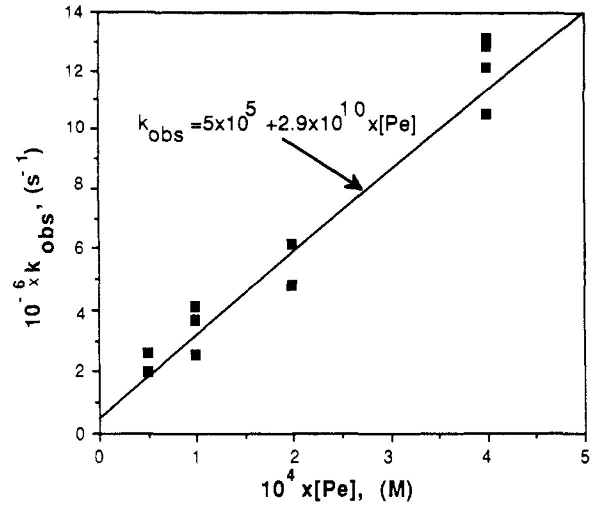

Figure 5. Pseudo-first-order formation constants vs [Pe].

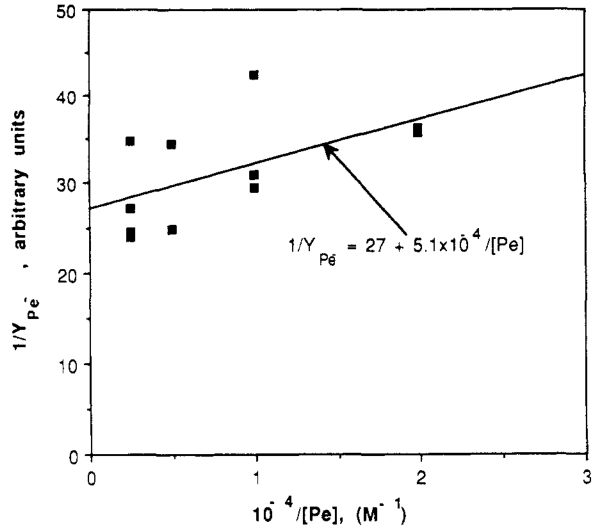

Figure 6. Dependence of the yield of the perylene radical anion formed by electron transfer from $CO_2^{\bullet -}$ on perylene concentration. The yield is in units of absorbance per 2 cm path length resulting from a pulse of 2.5 krad.

The yield of $Pe^{\bullet -}$ absorption as a function of [Pe] was also obtained from the fitting procedure. According to the above mechanism, the yields should follow eq II

$$1/Y_{Pe^{\bullet -}} = 1/Y_{Pe^{\bullet -},\infty}\{1 + k_0/(k_2[Pe])\} \qquad (II)$$

$Y_{Pe^{\bullet -}}$ is the relative yield of $Pe^{\bullet -}$ formed by reaction 1 and $Y_{Pe^{\bullet -},\infty}$ is the limiting yield at high [Pe]. (Note that this is not the yield one would actually measure at very high [Pe], but instead it is the yield obtained from the free ions plus the yield from geminate $CO_2^{\bullet -}$ scavenged by the maximum concentration of Pe used in these experiments.) A plot of $1/Y_{Pe^{\bullet -}}$ vs 1/[Pe] is shown in Figure 6. Because of the experimental scatter, the existence of a dependence of $Y_{Pe^{\bullet -}}$ on [Pe] is in doubt. However, a linear least-squares fit to the points in Figure 6 gives a slope to intercept ratio of k_0/k_2 = 1.9 × 10^{-5} M, which is consistent with the value of 1.7 × 10^{-5} obtained from the fitting procedure using the kinetics data, and a limiting absorption, $Y_{Pe^{\bullet -},\infty}$, of 0.037.

The limiting absorption $Y_{Pe^{\bullet -},\infty}$ would correspond to the yield of free ions if there were no appreciable problem due to geminate $CO_2^{\bullet -}$, as discussed earlier. By use of the known dose per pulse, $Y_{Pe^{\bullet -},\infty}$ can be converted to a value of the product $G_{Pe^{\bullet -}} \times \epsilon_{Pe^{\bullet -}}$ of 9 × 10^3 (with G in units of molecules per 100 eV and ϵ in units of M^{-1} cm^{-1}), where $G_{Pe^{\bullet -}}$ is the G value of $Pe^{\bullet -}$ formed by electron transfer from $CO_2^{\bullet -}$ and $\epsilon_{Pe^{\bullet -}}$ is the molar absorptivity of $Pe^{\bullet -}$ at

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580 nm. Because the 9-10-nm bandpass of the 580-nm interference filter is not negligible in comparison with the width of the 580-nm absorption band, this is an "effective" value of $\epsilon_{Pe^{\bullet -}}$. By use of a value of 5×10^4 M^{-1} cm^{-1} for $\epsilon_{Pe^{\bullet -}}$,[20] a value of 0.18 is obtained for $G_{Pe^{\bullet -}}$. This can be compared with G(free ions) in cyclohexane ≃0.15.[23] A value of $G_{Pe^{\bullet -}}$ greater than G(free ions) is expected because on a time scale of a few hundred nanoseconds the contribution of $CO_2^{\bullet -}$(geminate) + Pe → $Pe^{\bullet -}$(geminate) + CO_2 should be significant. Combined with the uncertainty in $\epsilon_{Pe^{\bullet -}}$, this precludes using the value of $G_{Pe^{\bullet -}}$ derived here as an accurate measure of G(free ions).

Conclusions

The experiments done here have shown that $CO_2^{\bullet -}$ transfers an electron to an aromatic system. In other words, it lengthens the lifetime of the electron that is formed in hydrocarbon radiolysis and can transfer it to electron-affinic species. Therefore, CO_2 would not be an appropriate electron-scavenging species in hydrocarbon radiolysis if its purpose were, for example, to prevent production of radical anions of an aromatic solute. However, if the aim were to slow down the geminate recombination while making the electron available for transfer to an aromatic molecule, CO_2 would be appropriate as an electron scavenger. Other information regarding CO_2 as an electron scavenger is that reaction of $CO_2^{\bullet -}$ with an aromatic radical cation has been observed to result in formation of the fluorescent state of the aromatic.[24]

The $CO_2^{\bullet -}$ ion is readily produced by pulse radiolysis, and the technique reported here can be used to make similar measurements for other solvents and solutes which exhibit a measurable radical anion absorption. A detailed study of this sort to determine the effects of electron affinity and solvent polarity on the transfer rate would be of interest.

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Registry No. Perylene, 198-55-0; carbon dioxide, 124-38-9; perylene radical anion, 34505-65-2; carbon dioxide radical anion, 14485-07-5.

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Kinetics of the Reactions of C_2H with C_2H_2, H_2, and D_2

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Kinetics of the reactions $C_2H + C_2H_2 \rightarrow C_4H_2 + H$ (1), $C_2H + H_2 \rightarrow C_2H_2 + H$ (2), and $C_2H + D_2 \rightarrow C_2HD + D$ (3) have been studied at $T = 293$ K with two time-resolved diagnostics, laser-induced fluorescence (LIF) detection of H (or D) atoms at the Lyman-α wavelength and mass spectrometric detection of C_4H_2. The C_2H radical was prepared by the ArF (193 nm) laser photolysis of C_2H_2. Measurements of the yield of H (or D) atom indicated that the C_2H radicals produced by the photolysis were converted effectively to H (or D) atoms; i.e., formation of the stable intermediates such as C_4H_3, C_2H_3, or C_2HD_2 was negligible under the present experimental conditions (p = 30 Torr). Rate constants of $k_1 = (1.6 \pm 0.1) \times 10^{-10}$, $k_2 = (7.1 \pm 1.1) \times 10^{-13}$, and $k_3 = (2.0 \pm 0.3) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} were derived from the pseudo-first-order rise rates of the H (or D) atom. Rate constant of $k_1 = (1.4 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} was also obtained at p = 5 Torr by measuring the appearance rate of C_4H_2. The ratios of the rate constants $k_2/k_1 = (3.4 \pm 0.2) \times 10^{-3}$ and $k_3/k_1 = (1.4 \pm 0.5) \times 10^{-3}$ were deduced by measuring the dependence of the C_4H_2 production on the partial pressure of added H_2 or D_2. Transition state theory calculations on the basis of ab initio transition-state properties demonstrated the importance of the tunnel effect for reaction 2 at room temperature.

1. Introduction

The reactions of the ethynyl radical, C_2H, are of considerable interest because of their importance in several chemical systems. The C_2H radical is known to be an important precursor to soot formation in the pyrolysis of C_2H_2.[1] It was also detected in interstellar space.[2]

The rate constants for the C_2H reactions with C_2H_2 and H_2

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H \qquad (1)$$

$$C_2H + H_2 \rightarrow C_2H_2 + H \qquad (2)$$

have previously been measured at room temperature by several groups. However, there exist serious discrepancies among the

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