of aqueous HPMS which might be formed in a polluted open atmosphere was calculated by assuming a concentration of 0.2  $\mu$ M free benzaldehyde, a SO<sub>2</sub> partial pressure,  $P_{SO_2}$ , of 20 ppb, and a pH of 4.0. A  $P_{SO_2}$  of 20 ppb is common in some urban areas. The benzaldehyde concentration was chosen from the highest values cited for Los Angeles rainwater by Kawamura and Kaplan,<sup>2</sup> although it is not clear whether their analytical method measures free or total benzaldehyde. Our estimate would overpredict potential HPMS concentrations if complexed benzaldehyde was also detected by their analysis. A free aqueous benzaldehyde concentration calculated on the basis of a gas-phase-liquid equilibrium assumption leads to comparable concentrations. Solving the following equations for [HPMS]

$$[HSO_3^-] = \frac{P_{SO_2}H_{SO_2}K_{a1}}{\{H^+\}}$$
(30)

$$[HPMS] = K_{HPMS}[C_6H_5CHO]_{free}[HSO_3]$$
(31)

where  $H_{SO}$ , (1.26 M atm<sup>-1</sup> at 25 °C) is the Henry's law constant for SO<sub>2</sub>, yields [HPMS] = 5.8 nM. This calculation indicates that only a small fraction of the benzaldehyde and S(IV) would be present as the adduct. The contribution of benzaldehyde to the speciation of S(IV) in atmospheric water droplets will be less important than that due to formaldehyde since benzaldehyde is less abundant and its adduct is less stable. Further research on other carbonyl-S(IV) systems is under way.

Acknowledgment. We gratefully acknowledge the Electric Power Research Institute (RP1630-47) and the Environmental Protection Agency (R811496-01-1) for providing financial support for this research. We also thank Drs. Detlef W. Bahnemann, Eric A. Betterton, and the reviewers for their helpful insight.

Registry No. p-MeOC<sub>6</sub>H<sub>4</sub>CHO, 123-11-5; p-MeC<sub>6</sub>H<sub>4</sub>CHO, 104-87-0; PhCHO, 100-52-7; p-ClC<sub>6</sub>H<sub>4</sub>CHO, 104-88-1; p-HOC<sub>6</sub>H<sub>4</sub>CHO, 123-08-0; p-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CHO, 555-16-8; sodium bisulfite, 7631-90-5; sodium sulfite, 7757-83-7.

# The Absolute Kinetics of Several Reactions of Substituted Diphenylcarbenes<sup>1a</sup>

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4,4'-Dibromo-, 4-bromo-, 4,4'-dichloro-, 4-chloro-, 4-methyl-, 4,4'-dimethyl-, 4-phenyl-, 4-carbomethoxyl-, 4-cyano-, 4cyano-4'-methyl-, and 4,4'-dimethyldiphenyldiazomethane were studied by laser flash photolysis. Excitation of the diazo compounds at 308 nm produced the corresponding diarylcarbenes. The kinetics of the reaction of the substituted carbenes with alkanes and methanol were examined. Hydrogen abstraction rates are largely insensitive to ring substitution, while the methanol reaction is accelerated considerably by p-methyl substitution and retarded by a para electron-withdrawing substituent.

Physical organic chemists have traditionally used substituent effects to probe the mechanism of a reaction. This is certainly true in the area of carbene chemistry where numerous workers have employed relative rate measurements in this regard.<sup>3</sup> Reports of substituent effects on the absolute kinetics of carbenes are rare. Closs and Rabinow reported on the kinetics of dimerization of diphenyl-, 4,4'-dibromodiphenyl-, and 4,4'-dimethyldiphenylcarbene;<sup>4</sup> they also measured the absolute rate constants for reaction of all three carbenes with 1,3-butadiene. The rate constant was found to be invariant with substituent being (6  $\pm$ 2)  $\times$  10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup> for all three carbenes. Closs has also studied the hydrogen atom abstraction reactions of four halo derivatives of diphenylcarbene with toluene by CIDNP. Turro and Moss have systematically varied the substituent pattern of phenyl halocarbenes and measured their reactivity toward olefins.<sup>5</sup> Miller and Shechter have studied the kinetics of thermal decomposition of substituted diphenyldiazomethanes.<sup>6</sup> Substitutent effects on

TABLE I:	Absorption Maxim	a for Substituted	I Diphenylcarbenes	and
Their Corr	esponding Benzhydry	yl Radicals		

		$\lambda_{max}$			
R	R′	carbene	radical	$\tau_{\rm G},\mu{ m s}$	
Н	Н	314	334 (335) <sup>c</sup>	1.5ª	_
Н	Br	321 (316) <sup>d</sup>	340	2.1ª	
Br	Br	330 (335) <sup>c</sup>	350 (350) <sup>c</sup>	1.6 <sup>a</sup>	
н	Cl	$321 (311)^d$	338	$2.0^{a}$	
Cl	Cl	322	345	2.1ª	
CH <sub>3</sub>	CH <sub>3</sub>	323	340	1.2ª	
CH <sub>3</sub>	CN	300	355-370	3.8ª	
-				5.9 <sup>b</sup>	
Н	CN	295	350-380	5.4ª	
				7.2 <sup>b</sup>	
Н	CO <sub>2</sub> CH <sub>3</sub>	295	370	$5.0^{b}$	
н	Ph	350	380	7.8ª	

<sup>a</sup>Cyclohexane. <sup>b</sup>Isooctane. <sup>c</sup>Closs, ref 4. <sup>d</sup>Trozzolo, ref 7.

the EPR and emission spectra of various diphenylcarbenes have been reported by Trozzolo and Gibbons and by Ware.<sup>7</sup> In this work we report the absolute kinetics of reactions of various diphenylcarbene derivatives with cyclohexane and with methanol.

#### Experimental Section

In a typical experiment a deaerated solution of  $5 \times 10^{-5}$  M diazo compound was subjected to laser flash photolysis (308 nm,  $\simeq 4$ 

<sup>(1) (</sup>a) Issued as NRCC No. 25528. (b) Ohio State University. (c) National Research Council of Canada.

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TABLE II: Bimolecular Rate Constants for the Reaction of Several Para-Substituted Diphenylcarbenes with Methanol at 300 K

R	R′	solvent	$k_{\rm q}, 10^6 {\rm M}^{-1} {\rm s}^{-1}$	$\lambda_{obsd}(max), nm$	_
Н	Н	cyclohexane	$12 \pm 1^{a}$	321	
Н	Br	cyclohexane	$5.1 \pm 0.6$	340	
		cyclohexane	$3.0 \pm 0.2$	321	
Н	Br	isooctane	$3.4 \pm 0.5$	321	
Br	Br	cyclohexane	$2.0 \pm 0.8$	350	
		cyclohexane	$2.3 \pm 0.2$	321	
Br	Br	isooctane	$6.5 \pm 1.4$	330	
		isooctane	$4.5 \pm 1.4$	321	
Н	Cl	cyclohexane	$6.9 \pm 0.8$	338	
		cyclohexane	$2.5 \pm 0.7$	321	
Н	Cl	isooctane	$2.8 \pm 0.4$	321	
Cl	Cl	cyclohexane	$2.9 \pm 0.3$	340	
		isooctane	$8.1 \pm 0.8$	322	
CH3	CH3	cyclohexane	104 ± 7	340	
		isooctane	$23 \pm 3$	323	
CH3	CN	cyclohexane	6.2	300	
Н	CN	cyclohexane	0.87	295	
Н	CO <sub>2</sub> CH <sub>3</sub>	cyclohexane	1.3	295	
Н	Ph	cyclohexane	7.9	350	
Н	CH3	isooctane	$36.1 \pm 15.0$	•	

<sup>a</sup> Errors are  $2\sigma$ . <sup>b</sup> The quenching plot shows some curvature.

ns, up to 80 mJ, Lumonics Model TE-860-2 operated with Xe-HCl mixtures) using a flow system. The absorption signals were captured by a Tektronix R-7912 transient digitizer and then transferred to a PDP 11/23 computer which also controls the experiment and provides suitable processing, storage, and hardcopy facilities. Further details of the laser flash photolysis system can be found elsewhere.<sup>8</sup> The diaryldiazomethanes used in this work were either known compounds or were prepared and purified from the corresponding benzophenones by known procedures.<sup>4,6,7</sup> The absorption maxima of the carbenes were typically recorded <0.5  $\mu$ s following laser photolysis. The methanol concentration range was selected so that the shortest lifetimes were 0.2–0.5  $\mu$ s.

### **Results and Discussion**

The carbene absorption maxima are in good agreement with the matrix isolation work of Trozzolo and Gibbons<sup>7</sup> and the flash photolysis work of Closs and Rabinow<sup>4</sup> where the data overlap. In cyclohexane as solvent the carbene spectra were found to decay with the concomitant increase of an absorption band at roughly 20 nm longer wavelength. The latter bands were assigned to the corresponding benzhydryl radical in analogy to our work with diphenylcarbene itself.<sup>9</sup> The rates of growth of the various benzhydryl radicals could be fit to a first-order process and led to the lifetimes given in Table I ( $\tau_G$ ). The lifetimes are all in the range of  $1.5 - 7.8 \ \mu s$ . In many cases the kinetics could be followed more cleanly using the benzhydryl radical growth than the carbene decay due to overlapping absorptions; the same had been observed for diphenylcarbene itself.<sup>9</sup>

The insensitivity of the hydrogen abstraction reaction to ring substitution is not entirely surprising. Our earlier work with diphenylcarbene (DPC) showed that its "radical-like" reactivity is intermediate between those for the methyl and phenyl radicals,<sup>9</sup> and much higher than typical reactivities for benzylic radicals such as Ph<sub>2</sub>CH. There is a virtual absence of polar substituent effects on the hydrogen abstraction reaction confirming the nonpolar nature of this atom transfer. The largest substituent effect observed was with 4-PhDPC. This is unsurprising as a para phenyl group can stabilize the reactive carbene orbital by  $\pi$  delocalization.

The mechanism of reaction of triplet carbenes with methanol to form a singlet ether is of considerable interest.

$$Ph_2C^{\uparrow\uparrow} + CH_3OH \rightarrow Ph_2CHOCH_3$$

This reaction necessarily involves a change in spin multiplicity. Closs and Rabinow,<sup>4</sup> following an earlier suggestion by Bethell,<sup>10</sup> proposed that the reaction proceeds via rapid singlet-triplet equilibration.

$$Ph_2C\uparrow\uparrow \xleftarrow{K} Ph_2C\uparrow\downarrow \xrightarrow{k_s} Ph_2CHOCH_3$$

In this model the observed rate constant  $(k_{obsd})$  for reaction of triplet diphenylcarbene with methanol would be

$$k_{\rm obsd} = k_{\rm s} K$$

This view has also been adopted by Turro and Eisenthal;<sup>11</sup> however, it has recently been criticized by Griller, Nazran, and Scaiano,<sup>12</sup> who measured the temperature dependence of the reaction and found that it was inconsistent with the proposed model and the available data. Three possible explanations were advanced:<sup>12</sup> (i) a surface crossing mechanism in which triplet diphenylcarbene reacts directly with methanol to yield singlet ground-state products, (ii) association with methanol significantly affecting the energy gap between spin states, leading to intersystem crossing within this complex and lower activation energy requirements than could have been anticipated, and (iii) the rather trivial explanation that the inconsistencies would dissapear if some of the reported kinetic data for the singlet carbene were incorrect. In fact iii has already been shown to be at least applicable to the values of  $k_{ST}$ , the intersystem crossing rate constant; recent work by Eisenthal's group has revised  $k_{\rm ST}$  in acetonitrile from  $9 \times 10^9$  to  $3 \times 10^9$  s<sup>-1</sup>.<sup>11,13</sup> However, this revision may not be enough to remove all the inconsistencies observed earlier.

It occurred to us that the examination of substitutent effects, including heavy atom effects, could throw some light on this question. The kinetics of reaction of various triplet carbenes were studied by following the growth of the corresponding benzhydryl radical ( $\lambda > 330$  nm) in cyclohexane and/or the decay of the carbene ( $\sim$ 321 nm). Our results have been summarized in Table II, where the second-order quenching rate constants  $(k_a)$  were obtained from

$$k = k_0 + k_a [CH_3OH]$$

where k is the observed pseudo-first-order growth rate constant at a particular methanol concentration and  $k_0$  is the rate constant for radical growth in the absence of methanol. The dependence of k on methanol concentration was found to be linear.<sup>14</sup> Much

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TABLE III: Arrhenius Parameters for Methanol Quenching of the Triplet State of Para-Substituted Diphenylcarbenes

R	R′	$E_{a}^{c}$ kcal/mol	$\log_{(A/M^{-1} s^{-1})^c}$	T range, K	$k_{300},^d$ M <sup>-1</sup> s <sup>-1</sup>
H	Н	$1.45 \pm 0.60$	8.35 ± 0.47	241-3264	$1.97 \times 10^{7}$
Br	Br	$2.02 \pm 0.28$	$8.33 \pm 0.24$	234-324ª	$7.20 \times 10^{6}$
CH <sub>3</sub>	CH,	$1.52 \pm 0.23$	$9.51 \pm 0.19$	236-328ª	$2.52 \times 10^{8}$
CH,	CN	$6.55 \pm 0.62$	$11.30 \pm 0.51$	250-316 <sup>b</sup>	$3.38 \times 10^{6}$
Н	CN	$6.13 \pm 0.51$	$10.46 \pm 0.42$	242-332 <sup>b</sup>	$9.89 \times 10^{5}$
Н	CO <sub>2</sub> Me	$6.19 \pm 1.04$	$10.60 \pm 0.81$	243-324 <sup>b</sup>	$1.24 \times 10^{6}$

<sup>a</sup>Acetonitrile solvent. <sup>b</sup>Isooctane solvent. <sup>c</sup>Errors are  $2\sigma$ . <sup>d</sup>Calculated from Arrhenius parameters.

to our surprise we find that *p*-methyl substitution drastically accelerates the reaction (compare first and last entries in Table II). We were rather concerned with this result, which led us to repeat it several times using diazo samples from different sources; these experiments make us quite confident that the rate enhancement observed is real. The same rates could also be obtained by monitoring the diazo bleach at 295 nm where the diazo and carbene (but not the benzhydryl radical) absorptions are very similar. By comparison with the mono- and dimethyl derivative all other carbenes examined show very small substitutent effects or actually retarded the rate of the methanol reaction. In a few cases the Arrhenius parameters for methanol quenching were determined (Table III). The dibromo derivative shows a slightly larger activation energy than the parent diphenylcarbene (although within the error limits), while the effect on the dimethyl derivative appears to result from an increased preexponential factor.

Ab initio calculations of singlet methylene generally agree that its lowest closed-shell electronic configuration has a filled in-plane " $\sigma$ " orbital and an empty out-of-plane p orbital (<sup>1</sup>A<sub>1</sub>).<sup>15</sup> The



open-shell singlet  $({}^{1}B_{2})$  is very much higher in energy than  ${}^{1}A_{1}$ . The lowest electronic state of methylene is the triplet  $({}^{3}B_{2})$ . The chemistry of singlet methylene is dominated by the electrophilicity of the empty orbital. Direct attachment of a substituent bearing a lone pair of electrons to the carbenic center greatly stabilizes the singlet  $({}^{1}A_{1})$  and can lower its energy below that of the corresponding triplet state.<sup>16</sup> Diphenylcarbene and many of its



derivatives are known to be ground-state triplets. While no ab initio calculations are available for diphenylcarbene it is reasonable to assume that singlet DPC is also a closed-shell species. The two phenyl rings in the triplet carbene do not lie in the same plane in the solid state, and probably not in solution due to unfavorable steric interactions.<sup>17</sup> This is most likely true for singlet diphenylcarbene as well and each ring can conjugate with mainly one of the nonbonding carbene orbitals. We expect that singlet diphenylcarbene has two noninteracting  $\pi$  systems, with electronic configurations resembling a benzyl cation and a benzyl anion centered on the same carbene carbon.

This viewpoint is strongly indicated by the work of Miller and Shechter<sup>6</sup> who measured the rate of thermal decomposition of substituted diphenyldiazomethanes. They found that both electron-donating and -withdrawing groups accelerated the thermal extrusion of nitrogen. These workers felt that the substituent effect has its origin in transition-state stabilization rather than in destabilization of the diphenyldiazomethanes. Significantly para,para' disubstitution with two electron-donating or two electron-withdrawing substituents was less effective than that of a single substituent at accelerating the decomposition of the diazo compound. However, a para,para' combination of an electrondonating and -withdrawing group on the same diazo compound was the most effective substitution pattern for accelerating the thermal decomposition of the diphenyldiazomethane. This is of course the stabilization pattern predicted for a closed-shell singlet carbene. Thus, this stabilization is reflected in a lowering of the transition state leading to the singlet carbene from the diazo precursor.

The preequilibrium model mentioned before predicts that  $k_{obsd}$ will be sensitive to the size of the singlet-triplet energy gap. Since the reaction of the singlet carbene with methanol is known to be approximately diffusion controlled, then the variations in overall kinetics would be simply a function of the triplet's ability to populate the singlet state. If the singlet carbene is a closed-shell species, then both electron-donating and -withdrawing substituents would be expected to lower the magnitude of the singlet-triplet energy gap. Thus, within the framework of a preequilibrium model both types of substituents should increase  $k_{obsd}$  for the reaction with methanol and a single substituent would be expected to be as efficient or more efficient than two identical para,para' substituents. Quite clearly this is not the pattern observed (Tables II and III).

We take the failure of the preequilibrium model to predict the general trends of substituent effects as a clear indication that this model cannot be generally applicable to the reactions of all substituted diphenylcarbenes with methanol. Particularly significant is the observation that *p*-methyl-*p*'-cyanodiphenylcarbene reacts with methanol more slowly than diphenylcarbene itself, since on the basis of Miller and Shechter's<sup>6</sup> study one would predict this to be an ideal substitution pattern. Interestingly, the observed rates of reaction with methanol fit a reasonable Hammet correlation for  $\sigma$  values with  $\rho \sim -2$ .

In earlier work on the temperature dependence of the reaction of diphenylcarbene itself with methanol we concluded that the preequilibrium model was not applicable because the experimental Arrhenius parameters were inconsistent with those that could be expected on the basis of this model.<sup>12</sup> Examination of the data in Table III indicates that the same arguments would be applicable to the dibromo and dimethyl derivatives. However, the values of activation energy and preexponential factors for the *p*-cyano and *p*-methyl-*p'*-cyano derivatives are approximately those that could be expected on the basis of a preequilibration model where the singlet and triplet states are in equilibrium and the singlet reaction approaches diffusion control.

The reaction of singlet diphenylcarbenes with methanol can be viewed as proceeding along three limiting pathways involving intermediates A, B, or C. These involve predominantly covalent



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interactions (A), electron transfer (B), or proton transfer (C). Naturally, the reaction may proceed by an intermediate between these extreme forms that is controlled by the ability of the system to develop charge at the carbon and oxygen atoms.

The reaction of a triplet carbene with methanol to give benzhydryl methyl ether necessarily involves intersystem crossing. Intersystem crossing will occur at a set of nuclear coordinates common to both the singlet and triplet surfaces. We propose that the data for alkyl- and halo-substituted diphenylcarbenes and diphenylcarbene itself is best interpreted as involving a tripletsinglet crossing point which resembles an intermediate such as C (on the singlet surface). Thus, donating substituents will facilitate reaction of the triplet with methanol allowing it to more easily intersystem cross to a structure such as C on the singlet surface. This higher crossing probability is reflected as an increase in the preexponential factor (see effect of dimethyl substitution in Table III). We also note that in this interpretation the effect of a second methyl substituent (see Table III) is expected to enhance the substituent effect observed on monosubstitution rather than offset the effect of the first methyl group as one would anticipate in a mechanism controlled solely by the energy gap. On the other hand, electron-withdrawing substituents (such as -CN or  $-CO_2CH_3$ ) will lower the energy of the singlet carbene relative to the triplet carbene but will raise the energy of that part of the singlet reaction surface resembling species C. The two effects of an electron-withdrawing substituent on different portions of the singlet surface may now favor the preequilibrium mechanism as in the case of the last three entries in Table III.

The proton-transfer transition structure interpretation of the data for unsubstituted diphenylcarbene also explains the small but finite CH<sub>3</sub>OH/CH<sub>3</sub>OD isotope effects on the reaction, and why Bethell<sup>10</sup> found that more acidic alcohols react more rapidly than less acidic ones with diphenylcarbene. Neither of these two facts can be readily explained by a mechanism involving a preequilibrium followed by diffusion-controlled singlet carbene reaction with alcohol.

It is important to note that our data does not indicate which mechanism is actually preferred for reaction of singlet diphenylcarbene with methanol. Our data indicates only that triplet diphenylcarbene can most easily cross to that portion of the singlet reaction surface which resembles proton transfer. A surface crossing as pictured above would involve the coupling of a covalent triplet to a zwitterionic singlet state. This is, in general, the most favorable type of structure for spin-orbit-assisted intersystem crossing according to the theory of Salem and Rowland.<sup>18</sup>



Registry No. Diphenyldiazomethane, 883-40-9; (4-bromophenyl)phenyldiazomethane, 1140-32-5; bis(4-bromophenyl)diazomethane, 20359-77-7; (4-chlorophenyl)phenyldiazomethane, 1140-33-6; bis(4chlorophenyl)diazomethane, 1143-92-6; bis(4-methylphenyl)diazomethane, 1143-91-5; (4-cyanophenyl)(4-methylphenyl)diazomethane, 100813-36-3; (4-cyanophenyl)phenyldiazomethane, 838-14-2; (4-carbomethoxyphenyl)phenyldiazomethane, 100813-37-4; 4-phenyldiphenyldiazomethane, 30905-13-6; 4-methyldiphenyldiazomethane, 20359-75-5; diphenylcarbene, 3129-17-7; (4-bromophenyl)phenylmethylene, 14845-79-5; bis(4-bromophenyl)methylene, 61242-60-2; (4-chlorophenyl)phenylmethylene, 14845-78-4; bis(4-chlorophenyl)methylene, 24436-61-1; bis(4-methylphenyl)methylene, 32076-77-0; (4-cyanophenyl)(4methylphenyl)methylene, 100813-38-5; (4-cyanophenyl)phenylmethylene, 64568-30-5; (4-carbomethoxyphenyl)phenylmethylene, 100813-39-6; 4-biphenylphenylcarbene, 14845-83-1; (4-methylphenyl)phenylmethylene, 14845-80-8; cyclohexane, 110-82-7; isooctane, 26635-64-3; methanol, 67-56-1.

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## Kinetics of the Gas-Phase Reaction NO + NO<sub>3</sub> $\rightarrow$ 2NO<sub>2</sub>

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The rate constant for the reaction NO + NO<sub>3</sub>  $\rightarrow$  2NO<sub>2</sub> was measured over the temperature range of 209-414 K by using laser-induced fluorescence detection of NO<sub>3</sub> in a flow tube reactor. Our recommended results are  $k(T) = (1.55 \pm 0.23)$ ×  $10^{-11} \exp[(195 \pm 39)/T]$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for  $T \le 300$  K and  $k(T) = (2.95 \pm 0.27) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for T> 300 K. These two expressions were required to describe the observed non-Arrhenius behavior of k(T).

### Introduction

The role of the nitrate free radical  $(NO_3)$  in the chemistry of the earth's atmosphere has been recognized for some time.<sup>1-3</sup>  $NO_3$  has been measured in the stratosphere<sup>4,5</sup> and the troposphere,<sup>6-11</sup> and its atmospheric behavior has been modeled.<sup>12-16</sup> There are compounds<sup>12</sup> and many such reactions have been studied in the laboratory.<sup>17-23</sup>

The kinetics and photochemistry of the  $NO_{x}-O_{3}-N_{2}O_{5}$  system of which  $NO_3$  is an important constituent have been studied by several investigators.<sup>24-30</sup> However, little data has been available on the kinetics of the fundamental reaction

$$NO + NO_3 \rightarrow 2NO_2$$
 (1)

and until very recently the accepted rate constant was k(297 K)=  $(1.9 \pm 0.4) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> which was inferred from

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