

EFFECTIVENESS OF THE SCAVENGING ACTION OF NO IN VACUUM UV PHOTOLYSES OF C₂H₅Br: 121.6 - 193.1 nm REGION

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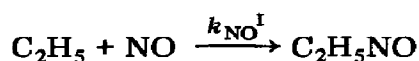
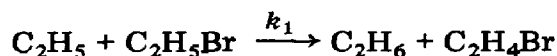
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Summary

The radical scavenging effect of NO, in the system of C₂H₅Br photolyses in the vacuum UV region, has been studied as a function of the energy content of C₂H₅ radicals and of the irradiation time.

C₂H₆, one of the principal reaction products, from the primary radical process in the system can be completely suppressed by adding the appropriate amount of a radical scavenger, *e.g.* NO at greater than 0.1 Torr. However, by adding an unsuitable amount of NO, *e.g.* 0.02 Torr of NO and 50 Torr of C₂H₅Br, the reaction between the C₂H₅ radical and NO becomes competitive with that of the C₂H₅ radical and C₂H₅Br by the following mechanism:



where R represents the C₂H₅ or C₂H₄Br radical.

The competitive reaction ratio between the C₂H₅Br/C₂H₅ and NO/C₂H₅ systems was obtained as a function of the irradiation energies with the variation in irradiation time by observing the production of C₂H₆. The values of $k_{\text{NO}}^{\text{I}}/k_1$, deduced by comparing the observed and the theoretical values, were found to be 4.0×10^3 at 121.6 nm, 9.5×10^3 at 147 nm, 14.0×10^3 at 163.3 nm, 17.0×10^3 at 174.3 - 174.5 nm and 23.0×10^3 at 193.1 nm.

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1. Introduction

Our recent studies on the vacuum UV photolyses of C_2H_5Br [1 - 5] have shown the two-channel modes of reactions of the molecular elimination and the C-Br bond fission in the primary process. The latter mode of reaction associated with an $n-\sigma^*$ transition [6] has been effectively suppressed by adding an NO radical scavenger. Frequently, however, the scavenging actions of NO for C_2H_5 radicals have revealed competition with hydrogen atom abstraction from the parent molecule by the radical, depending on the concentration of NO.

In earlier studies on the scavenging action of NO on alkyl radicals, the studies have been carried out on the basis of an assumption of a one-to-one NO-radical relationship [7 - 9]. In more recent work on the photolytic reaction of azo compounds it has been shown that a single NO molecule could accommodate up to three alkyl radicals [10].

The quantitative interpretation of these works, however, has been somewhat impeded by the lack or uncertainty of kinetic data on the scavenging action in neat solution, including the wavelength variation of the irradiating light, the exposure time and the pressure effect of the reactant molecules.

In this paper we report more accurate mechanistic and rate data on the scavenging action by NO for C_2H_5 radicals, by observations of the ratio between NO and C_2H_5Br competing for C_2H_5 radicals.

2. Experimental details

Photolyses were carried out at room temperature in a conventional static system, similar to that described previously [1 - 5]. Total conversions were held at less than 1% throughout the experiment. The light sources used in this work were hydrogen [11], xenon [1], bromine [12], nitrogen [2] and carbon [3] atom lamps powered by a microwave generator (KIVA Instruments Inc., model MPG-4M). The purity of the emission spectrum of each lamp was checked routinely with a 0.3 m GCA-McPherson 218 vacuum UV monochromator and some of the lamp characteristics are listed in Table 1.

Actinometry was based upon the production of $CH\equiv CH$ from the photolysis of $CH_2=CH_2$ ($\phi = 1.0$ at 121.6 and 147 nm, 0.7 at 163.3 nm, 0.75 at 174.3 - 174.5 nm and 0.4 at 193.1 nm) [13].

Product analysis was carried out using a gas chromatograph equipped with twin hydrogen flame ionization detectors (Hewlett-Packard, HP5840A) and confirmed using a gas chromatograph-mass spectrometer (Hewlett-Packard, HP5985B). The separation of the main product C_2H_6 was carried out using a 0.31 cm outside diameter \times 4 m 30% OV101/80-100 mesh Chromosorb PAW nickel alloy column at 80 °C and a carrier flow rate of 20 $cm^3 min^{-1}$.

TABLE 1
Light sources in vacuum UV region

Atomic species	Gas mixture	Wavelength of emission lines (nm)	Photon intensity used in this work (photons s ⁻¹)	Φ _R ^a
H	10% H ₂ in Ar	121.6	4.90 × 10 ¹⁴	0.41
Xe	20% Xe in Ar	147.0	2.76 × 10 ¹⁴	0.50
Br	0.5 ml Br ₂ + 1 Torr Ar	163.3	5.66 × 10 ¹⁴	0.60
N	20% N ₂ in Ar	174.3 - 174.5	1.59 × 10 ¹⁴	0.80
C	5% CH ₄ in Ar	193.1	1.81 × 10 ¹⁴	0.82

^aThe portion of the radical process occurring in the photolysis of C₂H₅Br (eqn. (R7)) at the given wavelength [1 - 3, 11, 12].

The quantitative analysis of C₂H₆ was performed by comparison of the retention time and the peak area of the product with that of the authentic sample. No attempt was made to analyse for nitroso compounds since the quantitative measurement of each nitroso compound has not been so successful even with time-of-flight mass spectrometry [7] and the equipment we have used in this study was not sensitive enough to detect them. Instead, the reduction in C₂H₆ yield was monitored as a function of irradiation time. The relative rate constants, *i.e.* k_{NO^i}/k_1 where $i = \text{I, II and III}$, were then deduced from the computer-simulated values by fitting to the monitored values of C₂H₆.

C₂H₅Br (stated purity greater than 98%) obtained from the Aldrich Chemical Co. was purified by gas chromatography (Perkin-Elmer, Sigma 4B) using a 0.63 cm outside diameter × 4 m 20% SE30/80-100 mesh Chromosorb P stainless steel column at 55 °C. NO (stated purity greater than 99.0%), obtained from Matheson, was used after trap-to-trap distillation at liquid nitrogen temperature.

3. Results

Table 2 summarizes the product yields, C₂H₆, in terms of pressure variations, for five different light sources. Also listed are the pressure of the reactant C₂H₅Br, the additives, *i.e.* NO and CO₂, and the irradiation times. In line numbers 1 - 8 of Table 2 the product C₂H₆, at the fixed irradiation time of 10 min, has shown a tendency to increase, from 10.1 to 15.8 mTorr, on variation of the reactant pressure from 9.3 to 97.8 Torr. It then reached a plateau of about 15 mTorr at 50 Torr of reactant pressure. This finding is interpreted as an indication that the reactant pressure, sufficient for the observation of the hydrogen atom abstraction reaction, is 50 Torr, considering the mechanism of C₂H₆ formation (see Section 4).

TABLE 2

C_2H_6 production *vs.* irradiation time in the photolysis of C_2H_5Br with or without additives in the vacuum UV region^a

Line number	Pressure (Torr) C_2H_5Br additives	Irradiation time (min)	C_2H_6 yield $\times 10^3$ (Torr) at given wavelengths (nm)				
			121.6	147	163.3	174.3	193.1
1	9.3	10			10.1		
2	9.9	10			10.2		
3	15.5	10			12.4		
4	33.8	10			14.5		
5	50.0	10			15.0		
6	68.5	10			14.3		
7	80.0	10			15.1		
8	97.8	10			15.8		
9	50.0	3		—	4.3	—	
10	50.0	4		0.96	—	—	
11	50.0	5		—	7.9	1.96	
12	50.0	7		—	10.7	—	
13	50.0	8		2.34	—	—	
14	50.0	10		—	—	3.75	
15	50.0	12		3.6	—	—	
16	50.0	15		4.7	22.4	5.51	
17	50.0	20		—	30.9	6.38	
18	50.0	30		—	—	9.15	
19	50.0 NO 0.02	2	1.6	0.25	—	—	0.16
20	50.0 NO 0.02	3	2.4	0.53	1.2	0.22	—
21	50.0 NO 0.02	4	—	—	—	—	0.28
22	50.0 NO 0.02	5	—	0.74	1.6	0.35	—
23	50.0 NO 0.02	7	3.9	0.94	—	0.55	0.61
24	50.0 NO 0.02	8	—	0.97	3.9	—	0.75
25	50.0 NO 0.02	10	—	1.50	5.8	1.05	0.93
26	50.0 NO 0.02	12	7.3	2.20	7.6	1.34	1.20
27	50.0 NO 0.02	13	8.7	2.80	—	—	—
28	50.0 NO 0.02	14	—	3.20	11.0	—	—
29	50.0 NO 0.02	15	—	—	—	1.90	—
30	50.0 NO 0.02	16	—	—	13.0	2.34	—
31	50.0 NO 0.02	17	—	—	—	—	2.40
32	50.0 NO 0.02	18	—	—	15.0	—	—
33	50.0 NO 0.02	19	—	4.60	—	—	—
34	50.0 NO 0.02	21	13.3	—	—	—	2.6
35	50.0 NO 0.02	22	—	5.80	—	—	—
36	50.0 NO 0.02	24	—	—	—	4.17	—
37	50.0 NO 0.02	28	19.3	—	—	—	—
38	50.0 NO 0.02	30	—	—	—	4.99	—
39	8.18 NO 0.02	10					0.31
40	8.18 NO 0.02	10					0.25
	CO ₂ 20.5						
41	8.18 NO 0.02	10					0.25
	CO ₂ 48.9						
42	8.18 NO 0.02	10					0.29
	CO ₂ 78.3						
43	8.18 NO 0.02	10					0.28
	CO ₂ 81.3						

^aThe blank spaces indicate that no experimental work at that wavelength was performed. The dashes indicate that the experiments were done at the wavelength but that no data were obtained at that particular condition.

Since the irradiation time required to consume the total amount of NO, 0.02 Torr as R_3NO , is a maximum of 20 min at the photon intensity 10^{14} photons s^{-1} , we also suggest that the optimal irradiation time for the competitive reaction is less than 20 min.

Line numbers 9 - 18 in Table 2 show that the formation of C_2H_6 , at 50 Torr of neat reactant, increased at a constant rate with increasing irradiation time for the 147, 163.3 and 174.3 - 174.5 nm photolyses. Line numbers 19 - 38 represent the effect of irradiation time in the presence of NO and at the five different wavelengths, indicating that the rate of C_2H_6 formation increased non-linearly with the irradiation time. The non-linearity

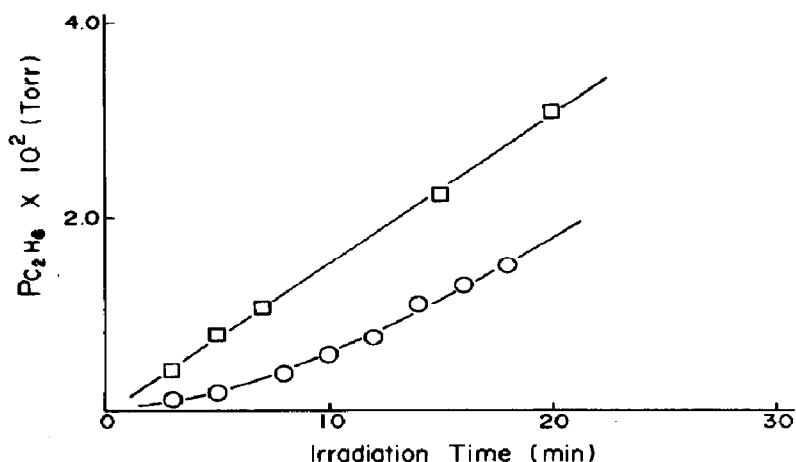


Fig. 1. C_2H_6 yield as a function of irradiation time with (○) or without (□) NO gas at 163.3 nm. The initial pressures of C_2H_5Br and NO were fixed at 50 Torr and 0.02 Torr respectively.

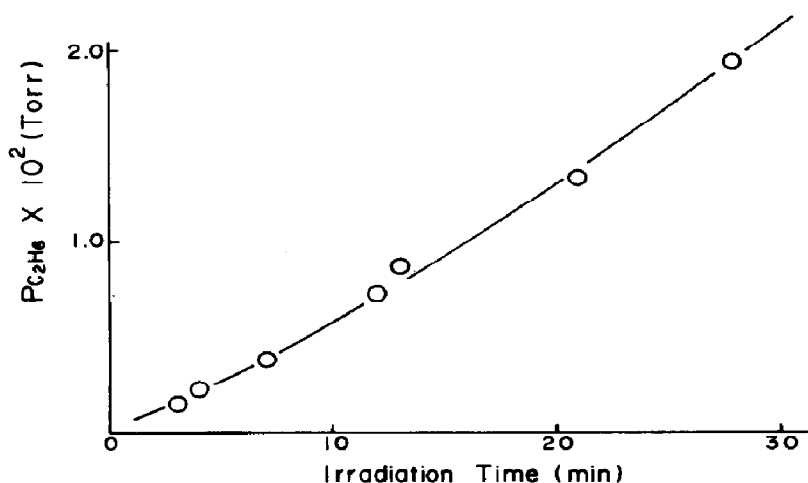


Fig. 2. Scavenger effect of NO gas in the production of C_2H_6 as a function of irradiation time at 121.6 nm. The initial pressures of C_2H_5Br and NO gas were fixed at 50 Torr and 0.02 Torr respectively.

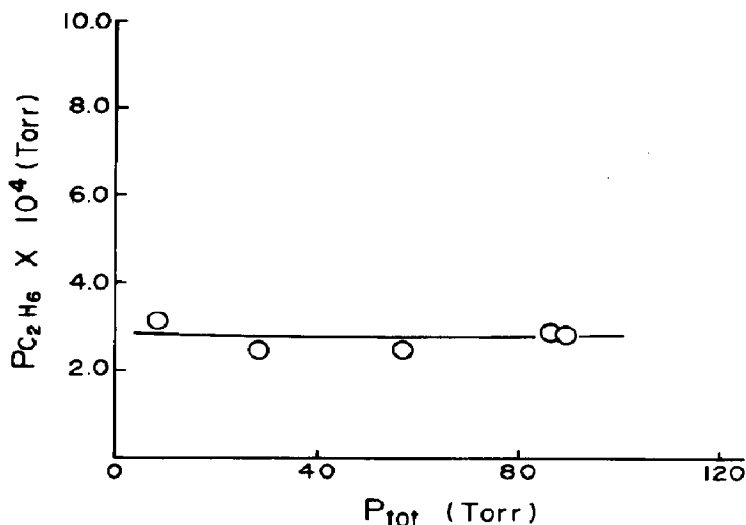


Fig. 3. Pressure effect of CO_2 on the scavenging action of NO gas in the production of C_2H_6 at 193.1 nm. The initial reactant pressures were 8.18 Torr of $\text{C}_2\text{H}_5\text{Br}$ and 0.02 Torr of NO .

of the curve was found to be dependent on the irradiation wavelength, *e.g.* Fig. 1 for 163.3 nm and Fig. 2 for the 121.6 nm photolyses.

Line numbers 39 - 43 in Table 2 represent the effects of CO_2 on the 193.1 nm photoreaction at the fixed pressures of the reactant, 8.18 Torr, and of NO , 0.02 Torr. The pressure effect was not observed in the pressure range 0 - 81.3 Torr of CO_2 as is displayed in Fig. 3.

4. Discussion

On the basis of the primary processes proposed, one of the electronically excited states $\text{C}_2\text{H}_5\text{Br}^{\dagger(1)}$ initially formed decomposes to C_2H_4 and HBr by molecular elimination while the other excited state $\text{C}_2\text{H}_5\text{Br}^{\dagger(2)}$ decomposes by C-Br bond rupture to yield a scavengeable C_2H_5 radical.



The possibility of cross over from $\text{C}_2\text{H}_5\text{Br}^{\dagger(1)}$ to $\text{C}_2\text{H}_5\text{Br}^{\dagger(2)}$, induced by collisions, has been suggested from time to time. However, in these systems this possibility has been ruled out for the following reasons. Since the calculated collision rate, assuming a collision diameter of 0.513 nm [14] for $\text{C}_2\text{H}_5\text{Br}$, is given by $\omega \text{ (s}^{-1}\text{)} = 9.113 \times 10^6 P \text{ (Torr)}$ at the total pressure P , and if the lifetime of $\text{C}_2\text{H}_5\text{Br}^{\dagger(1)}$ is taken to be the usual value

of about 4×10^{-10} s, then the required pressure of effective collision for E-E energy transfer is about 250 Torr. This value is far too high, considering our system pressure, which was less than 50 Torr.

Direct addition of hot C_2H_5 radicals to NO produces a vibrationally excited C_2H_5NO compound and the mechanism may be described by the following three elementary steps:



Line numbers 39 - 43 in Table 2 present the pressure effect of CO_2 on $C_2H_5NO^*$ species as shown in Fig. 3. However, the above mechanism does not fit our observations since the C_2H_6 yield was not affected by the total pressure increase.

From the observations in this and similar studies [10] we propose a mechanism in which an NO molecule accommodates up to three radicals at maximum. The initially formed C_2H_5NO undergoes secondary and tertiary reactions with radicals, as described in the following mechanism:



where R represents a C_2H_5 or C_2H_4Br radical.

From the mechanism given above the theoretical yield of C_2H_6 may be derived and this is described in Appendix A. For the following equation two assumptions were imposed: (a) C_2H_5 and C_2H_4Br radicals should have steady state concentrations during the photolysis; (b) the reaction rates of C_2H_5 and C_2H_4Br to give NO compounds should be the same in each case. The second assumption was made on the basis of the similar behaviour found experimentally for methyl and halogenated methyl radicals, see ref. 10 (Heicklen and Cohen) p. 275, $k = 1.6 \times 10^8$ l mol⁻¹ s⁻¹ for CH_3/NO , and p. 283, $k > 10^8$ l mol⁻¹ s⁻¹ for CF_3/NO systems.

$$\begin{aligned} d[C_2H_6]/dt &= k_1[C_2H_5][C_2H_5Br] \\ &= I\Phi_R \left(1 + \frac{k_{NO}^I[NO]}{k_1[EtBr]} + \frac{k_{NO}^{II}[RNO]}{k_1[EtBr]} + \frac{k_{NO}^{III}[R_2NO]}{k_1[EtBr]} \right)^{-1} \end{aligned}$$

where k_{NO}^I/k_1 , k_{NO}^{II}/k_1 , and k_{NO}^{III}/k_1 are constants corresponding to the first, second and third rate constant ratios respectively, and arbitrary values were used as the initial values for the iteration.

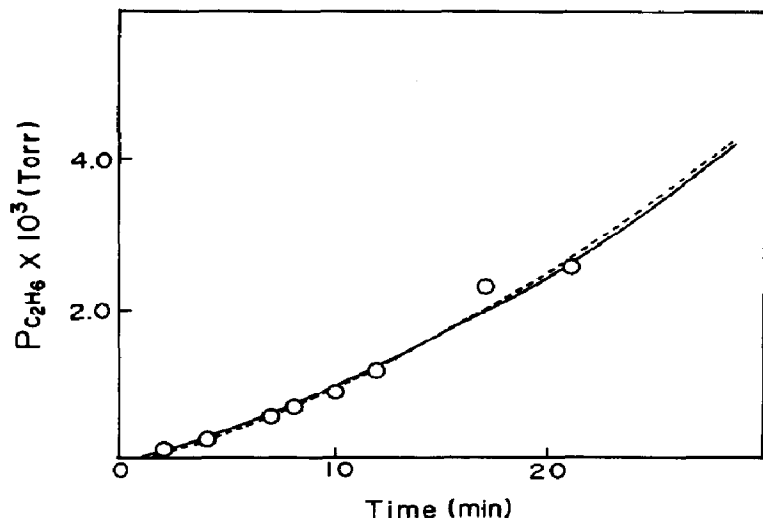


Fig. 4. Time dependence of C_2H_6 production with NO gas at 193.1 nm: —, theoretical C_2H_6 yield; - - -, least-squares fit curve; \circ , experimental C_2H_6 yield. The null hypothesis test was performed using the χ^2 test at $\alpha = 0.05$ and at each wavelength.

We obtained the theoretical yield of C_2H_6 by computer calculation and deduced the optimum k_{NO^i}/k_1 ($i = I, II$ and III) values by comparison with the observed yields of C_2H_6 . In Fig. 4 the simulated values at 193.1 nm, using our iteration technique, are displayed as a typical example. In order to check our hypothesis, we have performed the χ^2 null hypothesis test [15] and compared the theoretical curve with the non-linear least-squares curve using the program MINITAB (Minitab Inc.).

The energy dependence of the NO scavenging action was also investigated in terms of the k_{NO^i}/k_1 values, at five different vacuum UV wavelengths, in the same manner. From the deduced k_{NO^i}/k_1 values in Table 3 we know that the more internal energy the C_2H_5 radical contains, the less the scavenger effect of NO (*vide infra*). For example, k_{NO^I}/k_1 has been varied from 23.0×10^3 at 193.1 nm to 4.0×10^3 at 121.6 nm. In order to expand the energy dependence further to longer wavelengths and to test our proposed equation, we have extended the wavelength to 253.7 nm by extrapolation where the observed k_{NO} value of $2 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, by Christie and Frost [8], and the assumed k_1 value of $1.0 \times 10^5 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, in their computer simulation study of C_2H_5Br photolysis by Frank and Hanrahan [16], were available. Although our estimated value for k_{NO^I}/k_1 , i.e. 4.84×10^4 , was smaller than the computer-simulated value, i.e. 200×10^4 , the trend was found to be the same and supports strongly our proposal. Further, we were able to calculate the second and third rate constant ratios, i.e. $k_{NO^{II}}/k_1$ and $k_{NO^{III}}/k_1$, although these values were far less sensitive than the first rate constant ratio k_{NO^I}/k_1 for the calculation. It was shown that the ratio of the first rate constant to the second rate constant varied from 8 to 23 in this region which is in good agreement with the ratio for the

TABLE 3

Calculated first, second and third rate constant ratios of C_2H_5/NO to C_2H_5/C_2H_5Br

λ (nm)	H^a (Torr s ⁻¹)	A^b ($\times 10^3$)	B^c ($\times 10^2$)	C^d	A/B
121.6	1.90×10^{-5}	4.0	1.7	$> 10^4$	23
147.0	1.30×10^{-5}	9.5	5.6	$> 10^4$	17
163.3	3.20×10^{-5}	14.0	9.3	$> 10^4$	15
174.3 - 174.5	1.20×10^{-5}	17.0	14.2	$> 10^4$	12
193.1	1.40×10^{-5}	23.0	28.8	$> 10^4$	8

^aConversion parameter $H = I\Phi_R$ (I equals light intensity, Φ_R equals portion of radical process).

^b $A = k_{NO^I}/k_1$.

^c $B = k_{NO^{II}}/k_1$.

^d $C = k_{NO^{III}}/k_1$.

similar system of azomethane- d_6 photolysis at 366 nm and at room temperature, *i.e.* 15. The ratios in Table 3 (as A/B values) suggest that NO is more effective in scavenging C_2H_5 radicals than C_2H_5NO with the increasing internal energy of the C_2H_5 radical. Since the third rate constant ratios were very insensitive for the calculation, it may require additional work to find precise values. At present, our calculation indicates that the values range from 10^4 to 10^5 , with very small and inconclusive contributions to the calculation. Nevertheless, the large values may be attributed to the free radical properties of the R_2NO compound.

From the external photon energy of 148.1 (at 193.1 nm) to 235.2 kcal mol⁻¹ (at 121.6 nm), considering the endothermicity of the C_2H_5 radical formation reaction ($\Delta H = 69$ kcal mol⁻¹) and taking account of the bromine excitation energy (10.5 kcal mol⁻¹) by spin-orbit relaxation ($^2P^0_{3/2} - ^2P^0_{1/2}$) on the grounds of the experimental observations [17], the remaining energy, *i.e.* 68.6 - 155.7 kcal mol⁻¹, must be distributed to the relative translational (rotational) and internal degrees of freedom of the reaction products. Now, if the statistical theory is applicable to the present system, 3/18 of these energies must be distributed to the relative translational energy of the products, *i.e.* 13 - 27.7 kcal mol⁻¹, and mostly to the bromine atom. The average internal energy of a hot C_2H_5 radical is then expected to be 55.4 - 128 kcal mol⁻¹ for the system. Since these energies are much higher than the threshold energy (about 40 kcal mol⁻¹) for the decomposition of the C_2H_5 radical to form C_2H_4 and a hydrogen atom, the reaction shown below can also be suggested as a possible pathway



However, this possibility has been ruled out on experimental grounds, although eqn. (R12) is possible energetically. Our previous study [2] has shown that the presence of NO and the variation in total pressure has no effect on the quantum yield of C_2H_4 . Consequently, the reaction (eqn.

(R12)) cannot be considered to contribute significantly to the C_2H_4 yield and this also places an upper limit on the internal energy of C_2H_5 , making it below the threshold of about 40 kcal mol^{-1} , with a corresponding larger amount of the excess energy being channelled into translation of the radicals, the latter favouring eqn. (R8) [12]. Further, it is reasonable to say that the statistical theory does not satisfy the present system for energy partitioning.

For this system we may simply adopt a quantity invariant under a change in energy units, namely f_v the fraction of available energy in vibration [18], for an exoergic reaction to describe the energy partitioning

$$\langle f_v \rangle = \frac{\langle E_v \rangle}{E_A} = \int_0^1 f_v P(f_v) df_v \quad (2)$$

where $\langle E_v \rangle$ is the average vibrational energy and E_A is the energy available for distribution to the vibrational and the relative translational modes. We are able to obtain $\langle f_v \rangle$ for the 121.6 nm photolysis, *i.e.* $0 < \langle f_v \rangle \leq 40/155.7$. Since the probability density function $P(f_v)$ is a characteristic of the potential surface [18], $\langle f_v \rangle$ is also invariant for any available energy. Hence we are able to fix the upper limits of the vibrational energy content of a C_2H_5 radical at various wavelengths. These are 40 kcal mol^{-1} , $29.6 \text{ kcal mol}^{-1}$, $24.6 \text{ kcal mol}^{-1}$, $21.8 \text{ kcal mol}^{-1}$, and $17.6 \text{ kcal mol}^{-1}$ for the 121.6 nm, 147 nm, 163.3 nm, 174.3 - 174.5 nm and 193.1 nm photolyses respectively. From the foregoing discussion it may be safe to draw a conclusion that the vibrational energy content of a C_2H_5 radical is dependent on the irradiation energy and therefore the competition rate constant ratio, *i.e.* $\log(k_{NO}^i/k_1)$, is also a simple linear function of $\langle E_v \rangle$. These arguments are well supported by our observations (*vide supra*). However, since the precise value of $\langle f_v \rangle$ for our system is not known at the present stage, further work in measuring $\langle E_v \rangle$ directly is necessary for a more quantitative description.

By comparing the absorption coefficients of C_2H_5Br (the estimated values from the absorption cross-section data [19], *i.e.* 1392 at 121.6, 570 at 147, 137 at 163.3, 210 at 174.3 - 174.5 and $37 \text{ cm}^{-1} \text{ atm}^{-1}$ at 193.1 nm) with that of an NO molecule, which is $69 \text{ cm}^{-1} \text{ atm}^{-1}$ at 116.5 nm and decreases drastically with increasing wavelength [20], and considering the concentration ratio between C_2H_5Br and NO, *i.e.* 50/0.02, we need not consider any complicated reactions due to the excitation of NO molecules in these regions. Alternatively, the relative contribution of k_{NO}^i (where $i = I, II$ and III) and k_1 in eqn. (1) to A, B and C in Table 3 may be deduced by comparing the relaxation times τ of the energy transfer between two pairs of the reactions, *i.e.* C_2H_5 and NO, and C_2H_5Br and C_2H_5 . By substituting the known values of k_{NO} [8] and k_1 [16] and the partial pressures of NO and C_2H_5Br of the system into the relation $\tau_i = (RT/P_j)/k_i$ (where $i = NO$ or 1 and $j = NO$ or C_2H_5Br) we find that τ_{NO} and τ_1 are 4.65×10^{-3} s and 3.71 s respectively, at 253.7 nm. These findings may be interpreted to mean that, at 253.7 nm, k_{NO} is about 1000 times more affected by the

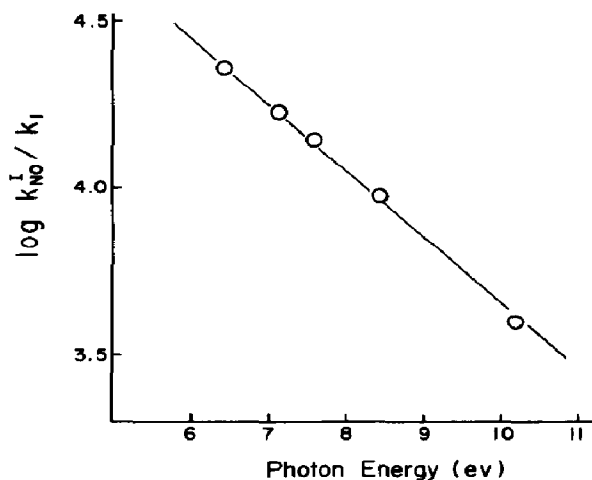


Fig. 5. Energy dependence of the NO scavenger effect in the C_2H_5Br photoreaction.

energy content of a C_2H_5 radical than k_1 and the same may be true at other wavelengths. Hence the term k_{NO}^I in eqn. (1) contributes more to A , B and C than k_1 in our system.

A most meaningful and important observation on the scavenging effect of NO is that the values of k_{NO}^I/k_1 in the vacuum UV wavelength region are strongly dependent on the irradiation energy as shown in Fig. 5. That is, the scavenging action increases linearly with decreasing internal energy of the C_2H_5 radical. In conclusion, we have proved that NO is a very effective radical scavenger in the vacuum UV region and that this effect is strongly related to the energy content of the C_2H_5 radical in the photolyses of C_2H_5Br .

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Appendix A: Evaluation of C₂H₆ formation

The time derivative of C₂H₅ radical concentration, utilizing eqns. (R7) - (R11), can be expressed by

$$\frac{d[\text{C}_2\text{H}_5]}{dt} = I\Phi_{\text{R}} - k_1[\text{C}_2\text{H}_5][\text{C}_2\text{H}_5\text{Br}] - k_{\text{NO}^{\text{I}}}[\text{NO}][\text{C}_2\text{H}_5] - k_{\text{NO}^{\text{II}}}[\text{C}_2\text{H}_5][\text{RNO}] - k_{\text{NO}^{\text{III}}}[\text{C}_2\text{H}_5][\text{R}_2\text{NO}] \quad (\text{A1})$$

and applying the steady state approximation to the C₂H₅ species and rearranging eqn. (A1)

$$[\text{C}_2\text{H}_5] = \frac{I\Phi_{\text{R}}}{k_1[\text{C}_2\text{H}_5\text{Br}] + k_{\text{NO}^{\text{I}}}[\text{NO}] + k_{\text{NO}^{\text{II}}}[\text{RNO}] + k_{\text{NO}^{\text{III}}}[\text{R}_2\text{NO}]} \quad (\text{A2})$$

The formation of an R radical is also, from eqns. (R7) - (R11)

$$[\text{R}] = [\text{C}_2\text{H}_5] + [\text{C}_2\text{H}_4\text{Br}]$$

$$\frac{d[\text{R}]}{dt} = I\Phi_{\text{R}} - k_{\text{NO}^{\text{I}}}[\text{R}][\text{NO}] - k_{\text{NO}^{\text{II}}}[\text{R}][\text{RNO}] - k_{\text{NO}^{\text{III}}}[\text{R}][\text{R}_2\text{NO}] \quad (\text{A3})$$

applying the steady state approximation to the R species

$$[\text{R}] = \frac{I\Phi_{\text{R}}}{k_{\text{NO}^{\text{I}}}[\text{NO}] + k_{\text{NO}^{\text{II}}}[\text{RNO}] + k_{\text{NO}^{\text{III}}}[\text{R}_2\text{NO}]} \quad (\text{A4})$$

The formation of C₂H₆ from eqn. (R8) is given by eqn. (A5) and substituting eqn. (A2) into eqn. (A5)

$$\frac{d[\text{C}_2\text{H}_6]}{dt} = k_1[\text{C}_2\text{H}_5][\text{C}_2\text{H}_5\text{Br}] \quad (\text{A5})$$

$$= I\Phi_R \frac{k_1[\text{C}_2\text{H}_5\text{Br}]}{k_1[\text{C}_2\text{H}_5\text{Br}] + k_{\text{NO}^{\text{I}}}[\text{NO}] + k_{\text{NO}^{\text{II}}}[\text{RNO}] + k_{\text{NO}^{\text{III}}}[\text{R}_2\text{NO}]}$$

and rearranging

$$\frac{d[\text{C}_2\text{H}_6]}{dt} = I\Phi_R \left(1 + \frac{k_{\text{NO}^{\text{I}}}[\text{NO}]}{k_1[\text{C}_2\text{H}_5\text{Br}]} + \frac{k_{\text{NO}^{\text{II}}}[\text{RNO}]}{k_1[\text{C}_2\text{H}_5\text{Br}]} + \frac{k_{\text{NO}^{\text{III}}}[\text{R}_2\text{NO}]}{k_1[\text{C}_2\text{H}_5\text{Br}]} \right)^{-1} \quad (\text{A6})$$

The formation of RNO is from eqn. (R9) and substituting eqn. (A4) into eqn. (A7)

$$\frac{d[\text{RNO}]}{dt} = k_{\text{NO}^{\text{I}}}[\text{NO}][\text{R}] \quad (\text{A7})$$

$$= \frac{I\Phi_R}{1 + (k_{\text{NO}^{\text{II}}}[\text{RNO}]/k_{\text{NO}^{\text{I}}}[\text{NO}]) + (k_{\text{NO}^{\text{III}}}[\text{R}_2\text{NO}]/k_{\text{NO}^{\text{I}}}[\text{NO}])} \quad (\text{A8})$$

The formation of R₂NO is also from eqn. (R10) and substituting eqn. (A4) into eqn. (A9)

$$\frac{d[\text{R}_2\text{NO}]}{dt} = k_{\text{NO}^{\text{II}}}[\text{R}][\text{RNO}] \quad (\text{A9})$$

$$= \frac{I\Phi_R}{1 + (k_{\text{NO}^{\text{I}}}[\text{NO}]/k_{\text{NO}^{\text{II}}}[\text{RNO}]) + (k_{\text{NO}^{\text{III}}}[\text{R}_2\text{NO}]/k_{\text{NO}^{\text{II}}}[\text{RNO}])} \quad (\text{A10})$$

The formation of R₃NO is from eqn. (R11) and substituting eqn. (A4) into eqn. (A11)

$$\frac{d[\text{R}_3\text{NO}]}{dt} = k_{\text{NO}^{\text{III}}}[\text{R}][\text{R}_2\text{NO}] \quad (\text{A11})$$

$$= \frac{I\Phi_R}{1 + (k_{\text{NO}^{\text{I}}}[\text{NO}]/k_{\text{NO}^{\text{III}}}[\text{R}_2\text{NO}]) + (k_{\text{NO}^{\text{II}}}[\text{RNO}]/k_{\text{NO}^{\text{III}}}[\text{R}_2\text{NO}])} \quad (\text{A12})$$

The concentrations of NO, RNO, R₂NO and C₂H₆ for small time intervals, i.e. $d[\text{R}] = \lim_{\Delta t \rightarrow 0} (\Delta[\text{R}])$, are approximated by

$$[\text{C}_2\text{H}_6] = [\text{C}_2\text{H}_6]_0 + \Delta[\text{C}_2\text{H}_6] \quad (\text{A13})$$

$$[\text{NO}] = [\text{NO}]_0 - \Delta[\text{RNO}] \quad (\text{A14})$$

$$[\text{RNO}] = [\text{RNO}]_0 + \Delta[\text{RNO}] - \Delta[\text{R}_2\text{NO}] \quad (\text{A15})$$

$$[\text{R}_2\text{NO}] = [\text{R}_2\text{NO}]_0 + \Delta[\text{R}_2\text{NO}] - \Delta[\text{R}_3\text{NO}] \quad (\text{A16})$$

$$[\text{R}_3\text{NO}] = [\text{R}_3\text{NO}]_0 + \Delta[\text{R}_3\text{NO}] \quad (\text{A17})$$