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Photochemical Reactivity of Vinyl Chloride

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The Photochemical Reactivity of Vinyl Chloride

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1. Introduction

The formation of 'photochemical smog' in polluted atmospheres results from the oxidation of hydrocarbon substances in a photochemically initiated reaction involving oxides of nitrogen. The oxidation products characteristic of photochemical smog include oxidants (mainly ozone), aldehydes, CO, organic nitrogen compounds and nitric acid. The relative importance of the various hydrocarbons which are emitted into the atmosphere in producing photochemical smog in a given area depends on the rate at which they undergo photo-oxidation. Investigators have drawn up an empirical scale of reactivity which is based on the measurement of certain rate parameters for the oxidation of individual hydrocarbons in laboratory experiments, carried out under simulated atmospheric conditions. The parameters most widely used for comparison are

(a) the rate of conversion of NO to NO_2

(b) the rate of hydrocarbon consumption, and

(c) the rate of ozone formation

The following general order of reactivity has been established[1, 2]

Internal olefins > polysubstituted benzenes > terminal olefins > mono alkyl benzenes > paraffins

The reactivity of a given hydrocarbon may be ascertained by comparing measured values of the above parameters with those for other hydrocarbons which have known reactivity.

Recent theories concerning the mechanism of the hydrocarbon-NO_x photo-oxidation have suggested that the major free radical species involved in the initial attack on the hydrocarbon is the hydroxyl radical, OH. There is accumulating experimental evidence which confirms this. In particular the rate of OH reaction with aliphatic hydrocarbons corresponds closely to the empirically determined photochemical reactivity for both unsaturated and saturated compounds. Although a similar correspondence is found for atomic oxygen and ozone reaction with olefins, the reactivity of O and O_3 with saturated hydrocarbons is too slow

to account for the observed photochemical reactivities of this class of hydrocarbons.

In order to determine the photochemical reactivity of vinyl chloride two series of experiments have been carried out. Firstly, the rates of photo-oxidation of ppm concentrations of vinyl chloride, ethylene, propylene and trans-2-butene in the presence of 1 ppm NO in air were measured and the rates compared. Secondly, the reactivity of these four olefins with hydroxyl radicals was measured by a technique recently developed in these laboratories[3] which uses the photolysis of gaseous nitrous acid as a source of hydroxyl radicals.

2. Photo-oxidation Experiments

(a) Procedure

Mixtures containing part-per-million concentrations of olefins and nitric oxide in synthetic air were made up in a 200 l flexible bag constructed of Tedlar film. There was no detectable adsorption of olefins, NO or NO_2 on this material (loss rate $< 1\%\ hr^{-1}$). Ozone loss rates were measurable ($\sim 10\%\ hr^{-1}$) but not serious. The bag was irradiated by two banks of fluorescent lamps which had a broad spectral intensity in the blue-UV region (300 - 450 nm) with maximum intensity at 365 nm. The Tedlar film is transparent throughout this region. The light intensity was approximately 75% of that of natural sunlight (zenith L = 40°) in this spectral range, as measured from the rate of photolysis of NO_2 in pure nitrogen ($k_d(NO_2) \simeq 0.27\ min^{-1}$).

Synthetic air was made up by introducing 50 l breathing grade oxygen to the bag and filling to 240 l with nitrogen (oxygen free grade). The trace gases, olefins and NO were added to the N_2 stream during filling. After allowing ten minutes for thorough mixing, the mixtures were irradiated and the concentrations of the olefin, the oxides of nitrogen NO and NO_2 and the ozone was determined as a function of time. The relative humidity of the air in the bag was approximate 20 ± 3% and the temperature 22 ± 2°C.

Analysis of NO and NO_2 was carried out using a chemiluminescence NO_x analy

(TECO Model 12A). Ozone was measured on a Nederbragt type ethylene chemiluminescence ozone detector, and the olefins were measured by gas chromatographic analysis using a flame ionisation detector. The minimum detectable concentrations using each of these techniques was of the order of 1 ppb and the precision at the 1 ppm level was better than ± 5%.

Materials: Nitric oxide was taken from a standard mixture containing 118 ppm NO in N_2. Ethylene (99.8%), propylene (99%), trans-2-butene (99%) and vinyl chloride (99.9%) were taken from 'lecture bottle' cylinders (BDH Ltd). No impurity was detected either by gas chromatographic or infra-red spectroscopic analysis of the vinyl chloride.

(b) Results

A. Photo-oxidation of vinyl chloride in the presence of NO

Fig. 1 shows the concentration time curves for the reaction of 2.21 ppm C_2H_3Cl with 0.970 ppm NO under continuous irradiation. A typical, though rather slow, 'photochemical smog' type reaction is observed; after a short induction period, oxidation of NO to NO_2 commences with accompanying consumption of the vinyl chloride and as the NO is depleted, the concentration of ozone rises. Even after six hours irradiation, oxidation of NO was incomplete and only 26% of the vinyl chloride had been consumed. After prolonged irradiation (22 hours), 79% of the vinyl chloride had been consumed and the ozone concentration had increased to 0.60 ppm. Thus, significant ozone concentrations result from the photo-oxidation of vinyl chloride in air but only after a long period of irradiation.

B. Comparison of the rates of photo-oxidation of vinyl chloride with hydrocarbons

Similar experiments to those described above were carried out for ethylene, propylene and trans-2-butene with initial concentrations of 2.36, 1.67, 2.10 ppm respectively. Initial NO concentrations were 1.02,

0.91, 0.97 ppm respectively. Fig. 2 shows the concentration time curves for removal of NO and the olefins. Clearly the reactivities of trans-2-butene and propylene are much higher than that of vinyl chloride which is similar to ethylene. The absence of a noticeable induction period for NO oxidation with propylene arises from the presence of a higher initial concentration of NO_2 in this experiment ($(NO_2)_0$ = 0.10 ppm for C_3H_6 compared with $\lesssim$ 0.03 for the other hydrocarbons). The same order of reactivity is also evident from the plots for ozone formation shown in Fig. 3.

A quantitative comparison of the photochemical reactivity can be made on the basis of a number of parameters. For the present discussion we will consider the following:-

(A) The average rate of NO oxidation to 50% NO consumption

(B) The amount of reactant consumed after a given time (4 hours)

(C) The maximum rate of ozone formation

(D) The final ozone concentration after essentially complete oxidation of NO.

The numerical values for these parameters, estimated from the concentration time curves are given in Table I.

On the basis of parameter A, the reactivity of vinyl chloride is rather close to that of ethylene but in terms of hydrocarbon reaction rate (B) vinyl chloride oxidation is significantly slower. Both compounds are considerably less reactive than propylene and trans-2-butene. For all four substances the final ozone concentration was approximately the same, showing that the chlorinated hyddocarbon, vinyl chloride, can potentially produce as much ozone as the 'reactive' olefins but only after a much longer reaction time.

3. Hydroxyl Radical Attack on Vinyl Chloride

(a) Procedure

Mixtures containing $\sim$7 ppm gaseous nitrous acid together with approximately

0.3 ppm each of NO and NO_2, diluted in a N_2-O_2 mixture (2:1) were made up in the Tedlar bag. The mixture was drawn from this reservoir at a constant flow rate through a 27 cm^3 cylindrical photolysis cell irradiated with 330 - 380 nm light from a mercury arc source. The concentrations of NO, NO_2 and HNO_2 at the inlet and outlet of the cell were measured and the rates of formation of NO and NO_2 (R_{NO} and R_{NO_2}) in the photolysis determined. Successive aliquots of vinyl chloride (or other olefins) were then added to the mixture and the effect of increasing olefin concentration on R_{NO} and R_{NO_2} determined. The maximum extent of photolysis of HNO_2 was approximately 4%.

(b) Results

Fig. 4 shows the effect of added vinyl chloride on the rates of NO, NO_2 and total NO + NO_2 formation in the photolysis of HNO_2. The rates are normalised to unit HNO_2 concentration. It will be seen that the addition of increasing amounts of vinyl chloride leads to a fall in the rate of NO formation, an increase in the rate of NO_2 formation and a less pronounced decrease in the total rate $R_{NO + NO_2}$. Similar effects were also obtained for the hydrocarbons ethylene, propylene and trans-2-butene.

The mechanistic interpretation of the results in Fig. 4 is complex and subject to considerable uncertainty. However, on the basis of the following simplified scheme, the data can give an estimate of the relative reactivity of the added hydrocarbons with OH.

In the absence of additive the photolysis of HNO_2 proceeds by

$$HNO_2 = OH + NO \qquad (1)$$

$$OH + HNO_2 = H_2O + NO_2 \qquad (2)$$

Thus equal rates of NO and NO_2 formation are expected in the photolysis. The slightly lower rate of NO_2 formation with zero C_2H_3Cl shown in Fig. 4 is due to the side reaction of NO_2 with OH to give HNO_3 which was not measured. When a compound, R, is present which reacts with OH radicals, reaction (3) then competes with reaction (2), e.g.

$$OH + R \rightarrow \text{free radical product } P \qquad (3)$$

The free radical product from (3) reacts with molecular oxygen which is present in great excess to yield a peroxy radical which can oxidise NO to NO_2

$$(P)\dot{O}_2 + NO \rightarrow NO_2 + (P)\dot{O}$$

Some of the $(P)\dot{O}$ radicals may then be lost by recombination or undergo further reactions leading to the formation of NO_2. Some of the $(P)\dot{O}_2$ radicals may also be lost by recombination. The radical loss processes are reflected in the decline in the total rate $R_{NO + NO_2}$ with increasing additive (Fig. 4). In the simple case of R = CO, then $(P)\dot{O}_2$ and $(P)\dot{O}$ are HO_2 and OH respectively and it has been shown[3] that the above mechanism fits the observations for the photolysis of HNO_2–CO mixtures. Furthermore, the relative rate constants for OH reaction can be obtained from a plot of the equation:

$$\frac{\Delta_{NO} + \Delta_{(NO + NO_2)}}{\phi_1 - \Delta_{(NO + NO_2)}} = \frac{k_3[R]}{k_x[NO_x]} \triangleq \frac{k_3}{k_2}\frac{[R]}{[NO_x]}$$

where Δ_{NO} and $\Delta_{(NO + NO_2)}$ represent the differences between the $R_{NO}/[HNO_2]$ and $R_{NO + NO_2}/[HNO_2]$ values respectively in the absence and presence of additive, ϕ_1 is the dissociation rate of HNO_2, k_2 and k_3 are the rate constants for reactions (2) and (3) respectively* and $[NO_x] = [NO + NO_2 + HNO_2]$. Fig. 5 shows a plot of the data for vinyl chloride, C_2H_4, C_3H_6 and t-C_4H_8-2 according to equation (i). The slopes of the plots give a measure of the ratio k_3/k_2, i.e. the relative reactivity of the hydrocarbons with OH. The order of reactivity is the same as that found in the photo-oxidation experiments.

By using the value of k_2 previously determined[3], relative to the well known rate constant for the reaction of OH with CO, values of k_3 of 9.4×10^{-12} and 5.6×10^{-12} in cm^3 $molecule^{-1}$ s^{-1} units are derived for C_2H_4 and C_2H_3Cl respectively from the above slopes. Recent determinations of the absolute value of the rate constant for the reaction of OH with ethylene all lie in the region of 3×10^{-12} cm^3 $molecule^{-1}$ s^{-1}[4]. The apparently higher value obtained in the present analysis almost certainly arises because more than one NO molecule is oxidised in the reactions following the attack of OH on C_2H_4. A comparison of

*k_x is a "lumped" rate constant reflecting the ...

the k_3 values indicates a stoichiometry factor of about 3. The stoichiometry factor for vinyl chloride is unknown and therefore the rate constant value obtained can only be regarded as an upper limit. By analogy with ethylene the true value is probably a factor of 2 - 3 lower than the value given.

4. Comparison of Reactivity Data with Other Investigators

Table II shows a comparison of the relative reactivities of the substances under consideration with those obtained by other investigators which have been summarised by Altshuller and Bufalini[1]. The OH reactivity data are compared with those of Morris and Niki[4].

There is reasonably good agreement between the relative reactivities of the various substances based on A, the rate of NO oxidation and B, the consumption of reactant. The differences which are observed can probably be attributed to the different experimental conditions and measurement methods used in the various investigations. A close correspondence between relative reactivity toward OH and reactivity in the photochemical oxidation system is also evident. This correspondence has also been noted by Morris and Niki on the basis of their OH reaction measurements, with which the present estimates show good agreement considering the uncertainty in the stoichiometry mentioned above. It is also of interest to note that the reactivity of trichlorethylene is similar to that of vinyl chloride and ethylene.

5. Products of Vinyl Chloride Photo-oxidation

In the present study no investigation of the products of the photo-oxidation of vinyl chloride has been made. The nature of the expected major products may be deduced by analogy with ethylene for which the major products are formaldehyde, CO and CO_2. Thus fission of the C-C bond occurs in the oxidation reaction, and in addition to the other three products observed for C_2H_4, vinyl chloride would be expected to yield formyl chloride. Although formyl chloride has apparently never been isolated as a stable compound, it may be stable at very low concentrations

in air. Normally it decomposes to HCl and CO which will undergo further oxidation only slowly in the photochemical system.

6. Eye Irritation

While there is a strong correlation between the various chemical parameters used to characterise the reactivity of hydrocarbons in the photochemical system, no such correlation exists with the eye irritation index[2]. This is no doubt due to the widely differing lachrymatory effects of the products formed from quite similar starting materials. In the absence of experimental data, any attempt to assess the eye irritation index for vinyl chloride must therefore be largely speculative.

The only chlorinated compound for which the eye irritation index has been reported is trichloro-ethylene[1] and there is unfortunately some conflict between two separate investigations. Trichloro-ethylene lies between propylene and ethylene in photochemical reactivity and gives an eye-irritation index reported to be either somewhat greater than propylene[5] or somewhat less than ethylene[6]. Taking the more pessimistic value, thought to be more realistic because of the possible formation of the strongly lachrymatory compounds phosgene and formyl chloride (the latter also being a potential product of vinyl chloride), and taking into account the somewhat lower photo-reactivity of vinyl chloride observed in the present investigation, then the data suggests that the eye-irritation index for vinyl chloride should be similar to that for propylene. Heuss and Glasson[2] reported values of 0.3, 0.5, 1.2 and 3.0 for ethylene, trans-2-butene, propylene and 1,3-butadiene respectively, together with those for many other hydrocarbons. The eye-irritation was assessed by a panel after 4 mins. exposure as: none, light, moderate or severe and assigned numerical values of 0, 1, 2 and 3 respectively. It should be pointed out, however, that atmospheric measurements of eye irritants are almost an order of magnitude lower than laboratory concentrations resulting in equal eye-irritation, according to Schuck and Doyle[7] and there is much uncertainty surrounding the subject.

7. Conclusions

The results discussed above show that

(a) Vinyl chloride undergoes photo-oxidation in a similar manner to other hydrocarbon compounds when C_2H_2Cl-NO-air mixtures are exposed to UV radiation of wavelength and intensity similar to that of solar radiation near the earth's surface.

(b) The photochemical reactivity of vinyl chloride, as measured from a number of rate parameters in the photo-oxidation reaction and also from its reactivity toward OH radicals, is similar to or slightly less than ethylene. Vinyl chloride is, therefore, only a moderately reactive precursor to photochemical smog, being less reactive than propylene and higher olefins, but more reactive than the normal paraffins.

(c) The rate constant for the reaction of OH with vinyl chloride has an upper limit of 5.6×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 300°K. The true value is probably a factor of 2 - 3 lower than this.

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6. K.W. Wilson, G.J. Doyle, D.A. Hansen and R.D. Englert, Symposium of ACS Division of Organic Coating and Plastic Chemistry, New York, Sept. 1969. See also Environ. Sci. and Tech. 3, 896 (1969) and ibid p. 1224 together with Ref. 1 p. 48.

7. E.A. Schuck and G.J. Doyle, 'Photo-oxidation of Hydrocarbons in Mixtures Containing Oxides of Nitrogen and Sulphur Dioxide', Report No. 29, Air Pollution Foundation, San Marino, Calif. (1959) see also Ref. 1 p. 56.

TABLE I

Rate parameters in photo-oxidation of vinyl chloride and some hydrocarbons

Reactant	A $-d[NO]/dt$ (ppm/min x 10^2)	B % reactant consumed after 4 hours	C $(d[O_3]/dt)_{max}$ (ppm/min x 10^2)	D final $[O_3]$ (ppm)
Vinyl Chloride	0.31	13	>0.017 /	0.60 (1300 min)**
Ethylene	0.34	25	>0.17 /	0.47 (1300 min)
Propylene	1.40	88 (13)*	0.58	0.66 (240 min)
Trans-2-butene	3.0	>100 (75)*	3.75	0.73 (80 min)

* hydrocarbon consumed after 30 minutes

/ maximum rate not achieved during reaction time used

** time at which final ozone concentration measured.

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TABLE II

Relative photochemical reactivities*

Reactant	This work			Altshuller & Bufalini[1]		Morris & Niki[4]
	A NO oxidation	B reactant consumption	C OH reactivity	A NO oxidation	B reactant consumption	C OH reactivity
C_2H_4	0.25	0.28	0.29	0.4	0.1	0.1
C_3H_6	1.0	1.0	1.0	1.0	1.0	1.0
$t\text{-}C_4H_8\text{-}2$	2.1	5.8	~ 3.0	2	~ 6	4.2
C_2H_3Cl	0.25	0.15	0.17	-	-	-
C_2HCl_3	-	-	-	0.5	0.45	-

*Reactivities are relative to propylene which is arbitrarily set at unity.

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Fig. 1 Concentration time curves for the photo-oxidation of vinyl chloride in the presence of NO.

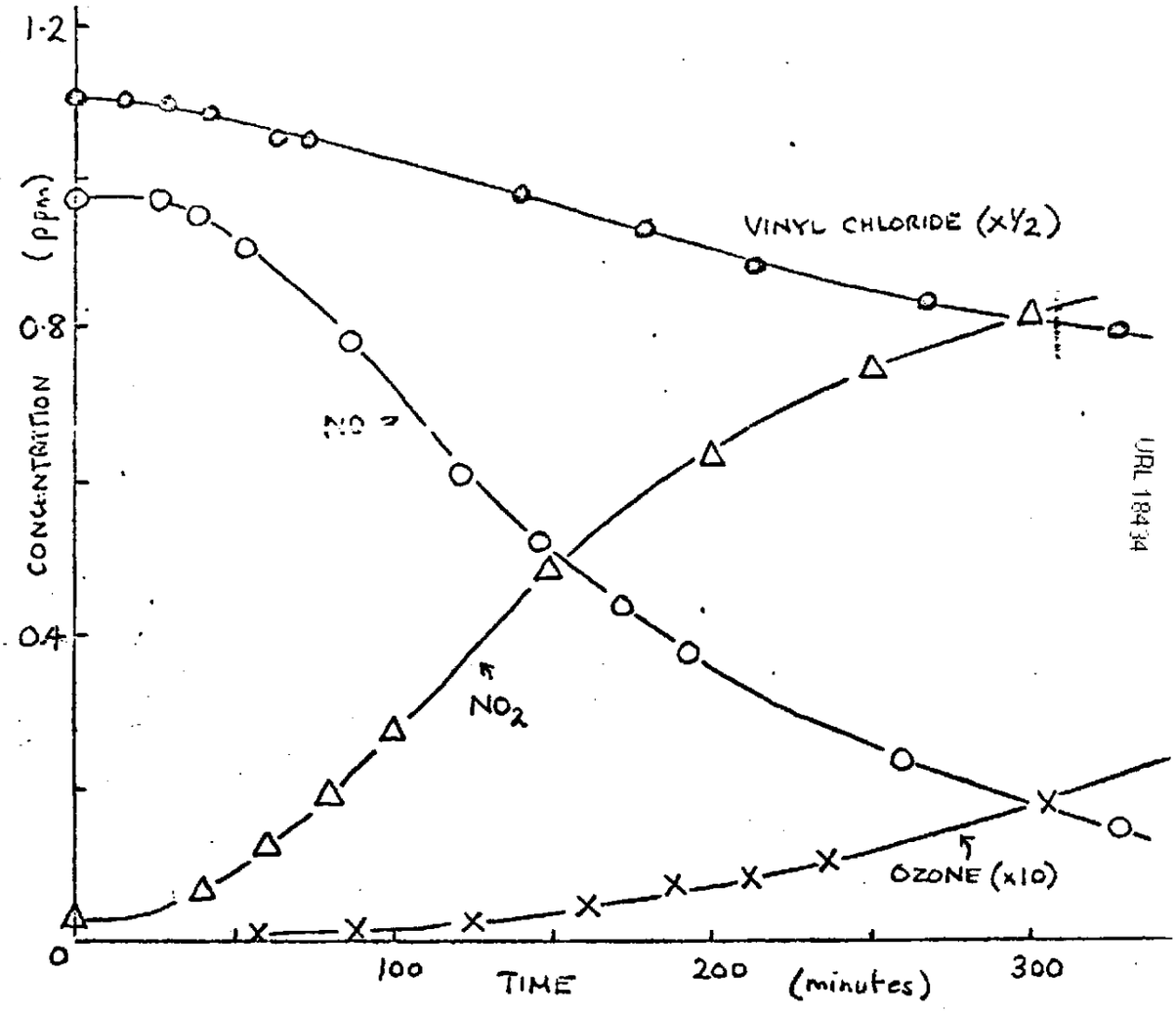

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Fig. 2 Plots showing the removal of olefin (filled points) and NO (open points) during the photo-oxidation of vinyl chloride (○), ethylene (△), propylene (□) and trans-2-butene (◇), in the presence of NO. The concentration axis for each hydrocarbon is shifted slightly so that the initial HC concentrations correspond to 0.97 ppm NO.

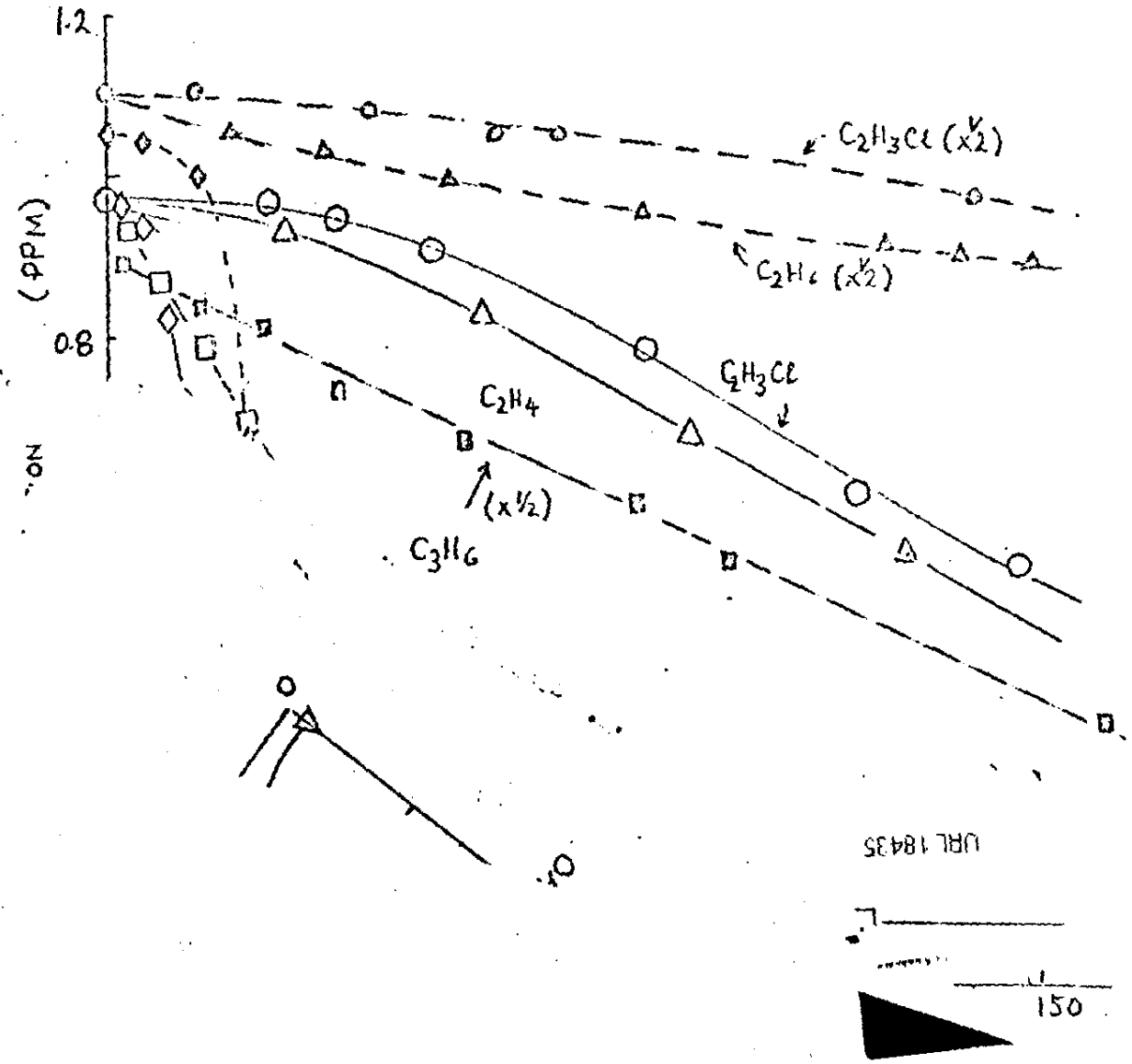

Fig. 3 Ozone formation during the photo-oxidation of hydrocarbons and vinyl chloride (filled points).

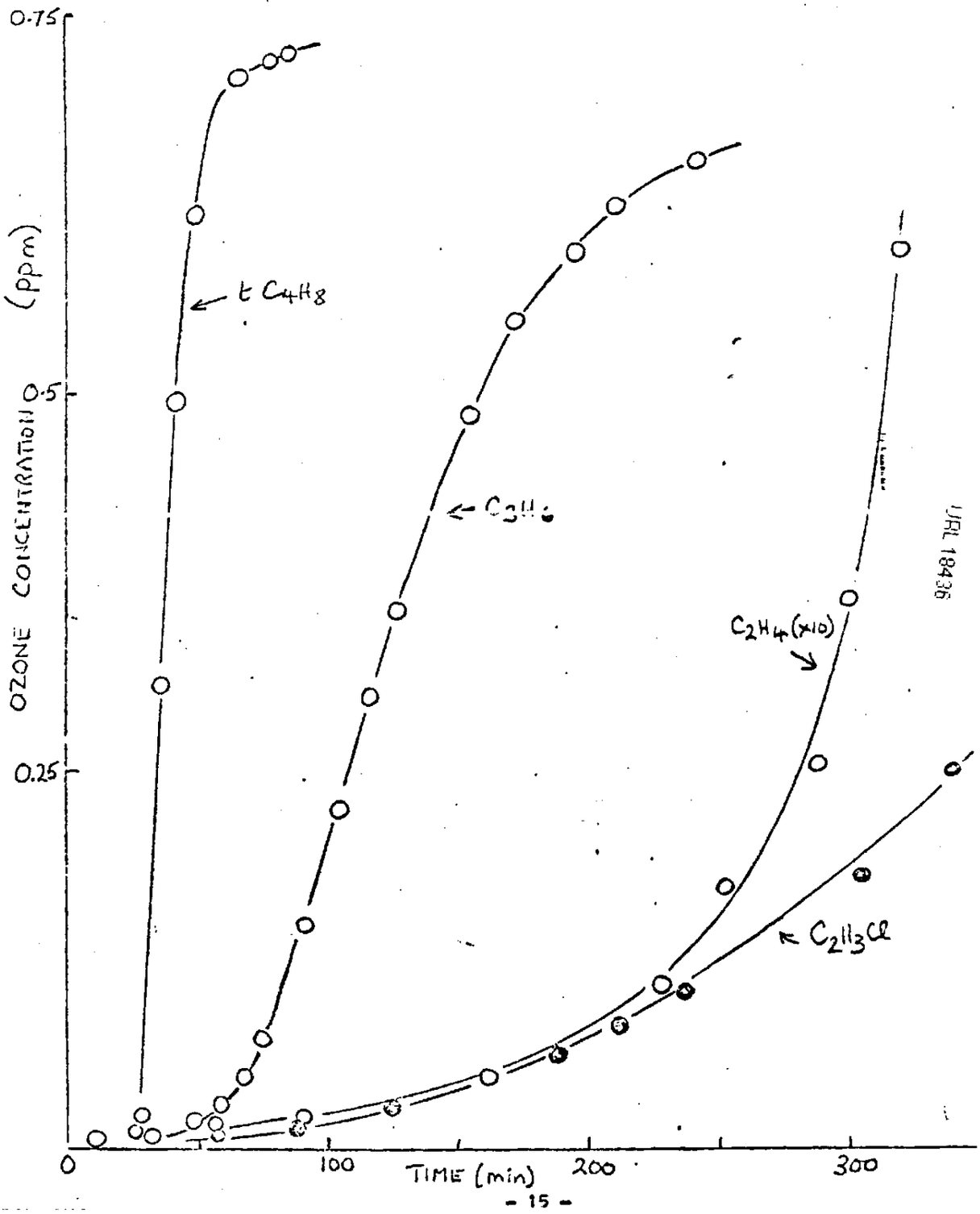

Fig. 4 The effect of added vinyl chloride on the photodissociation of nitrous acid. The plot shows the rates of formation of NO and NO_2 (R_{NO} and R_{NO_2}) and the total rate R_{NO+NO_2}, expressed per unit HNO_2 concentration as a function of the concentration ratio $[C_2H_3Cl]/[HNO_2]$.

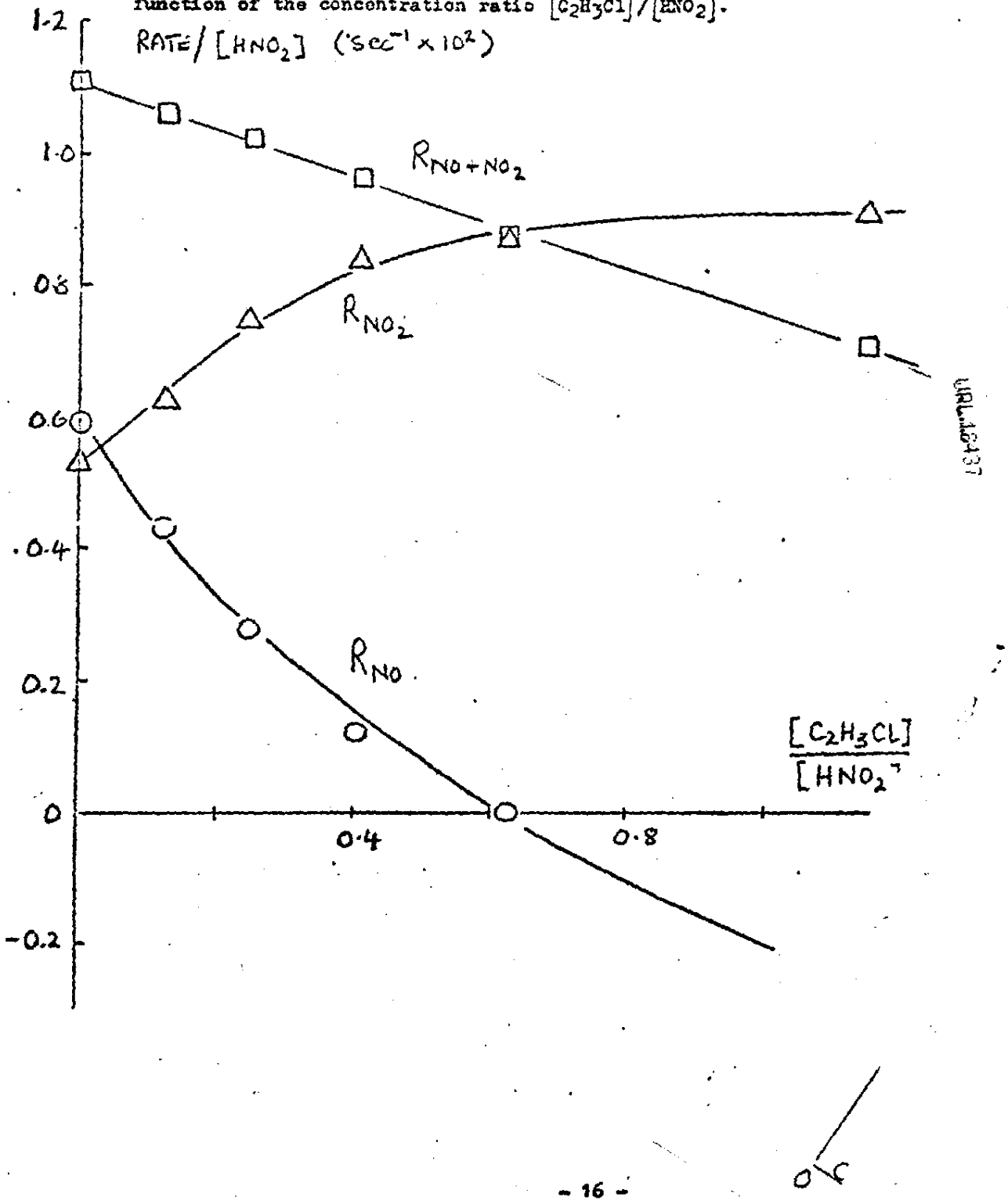

Fig. 5 Plot of the rate data from the photolysis of HNO_2-olefin mixtures according to equation (i) (see text).