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Air Pollution: Photooxidation of Aromatic Hydrocarbons

Abstract. A number of aromatic hydrocarbons participate as effectively as the olefins in atmospheric photooxidation reactions in the presence of nitrogen oxides and ultraviolet light. Judged both on the basis of reactivity and concentrations in the atmosphere, the aromatic hydrocarbons cannot be ignored as contributors to the photochemical type of air pollution.

When an olefin and nitric oxide, NO, in concentrations of parts per million (ppm) are exposed to ultraviolet radiation (>2900 Å) in the presence of oxygen, a rapid oxidation of NO occurs. This reaction is much more rapid than the thermal oxidation of NO by molecular oxygen in the same concentrations. Previous investigators, working with model systems, have usually studied only the hydrocarbons of the olefin series (*1, 2*).

However, Haagen-Smit (*3*) using rubber cracking as an index of ozone formation investigated the photooxidation of model mixtures of aromatic hydrocarbon and nitrogen dioxide, NO_2, systems. He found that appreciable rubber cracking occurred in mixtures containing xylenes and mesitylene. The photooxidation rates of NO in the presence of these aromatic hydrocarbons were not studied nor were their rates of reaction considered. In the present work both the photooxidation and the reaction rates of the aromatic hydrocarbon nitrogen oxide systems were investigated.

Mixtures in plastic bags containing 3 ppm of nitric oxide and 5 ppm of organic compound in a simulated atmosphere composed of 20 percent oxygen and 80 percent nitrogen were irradiated between two banks or warm-white, black-light, and sunlight type fluorescent lamps at a temperature of 36° to 38°C. The plastic was a copolymer of fluorinated ethylene and propylene. Colorimetric analyses for NO_2 were made at intervals during irradiation, which was continued until the NO_2 passed through maximum concentration and then began to decrease. The reactivity was expressed in terms of the average conversion rate at the time the NO_2 concentration reached one-half of its maximum value (half-conversion-time). The concentrations of ozone and of organic peroxy compounds were determined by the oxidation of iodide ion to triiodide ion in neutral solution. These concentrations were measured after irradiation times when the NO_2 concentration was substantially reduced. Corrections were made for the small amount of oxidation of the iodide solution by that NO_2 which remained in the reaction mixture.

The photooxidation of the mixtures of aromatic hydrocarbon and NO_2 were performed in an infrared cell adjusted for an optical path length of 80 m. A group of 72-inch warm-white and black-light fluorescent lamps lined the inner circumference of the cell. The temperature of the cell was about 45°C. The first order rate constant for NO_2 photolysis (K_d) as measured in the infrared cell was 0.2 per minute.

In this work the thermal rate of oxidation of NO by oxygen was measured at 3 ppm of NO and 0.05 to 0.1 ppm of NO_2 in 20 percent oxygen and 80 percent nitrogen. Values in the range of 0.005 to 0.007 ppm per minute were obtained repeatedly. Evidence for the participation of the organic hydrocarbons in the photooxidation of NO was based on reaction rates in excess of 0.005 to 0.007 ppm per minute.

The effect of ultraviolet light and 5 parts of aromatic hydrocarbons or olefins per million on the rate of oxidation of 3 parts of NO per million is given in Table 1. In the plastic containers, the K_d for NO_2 photolysis in nitrogen was 0.35 per minute. Net oxidant values expressed as parts per million by volume for ozone plus organic peroxycompounds are also listed for the more reactive aromatic compounds.

Table 1. Effect of organic hydrocarbons on the photochemically induced oxidation of nitric oxide to nitrogen dioxide.

NO_2		Oxidant	
Rate of formation*	Time to reach maximum (min)	Concn. (ppm)	Time obtained (min)
	Ethylene		
0.08	45		
	Propylene		
.18	20		
	Isobutene		
.20	23		
	Toluene		
.03	100	0.5	180
	p-*Xylene*		
.07	50	.65	150
	o-*Xylene*		
.07	50	1.0	130
	m-*Xylene*		
.17	25	0.85	90
	Mesitylene		
.22	17	1.1	150
	Isopropylbenzene		
.02	125		

* The rate is expressed as half-conversion time.

Summarizing the results, Table 1 clearly indicates that the most reactive aromatic hydrocarbons studied, such as 1,3,5-trimethylbenzene and *m*-xylene, participate in the photooxidation of NO at about the same rate as 1-alkenes. *O*-xylene and *p*-xylene reacted at about the same rate as ethylene. Monoalkyl derivatives such as toluene and isopropylbenzene participate much less than the dialkyl and trialkylbenzenes. This trend in reactivity for the aromatic hydrocarbons appears to be qualitatively related to their basicities and hyperconjugative order. The appreciable oxidant concentrations obtained strongly confirm the work of Haagen-Smit and Fox (*3*).

Preliminary infrared analyses indicate that the half-conversion times to products of the more reactive aromatic hydrocarbons such as 1,3,5-trimethylbenzene and *m*-xylene are somewhat less than the half-conversion time of about 4 hours for ethylene. Other moderately reactive aromatic hydrocarbons have half-conversion times equal to or somewhat less than that of ethylene. This result confirms a previous investigation of the irradiation of diluted auto exhaust mixtures in which aromatic hydrocarbons including the xylenes, styrene, and trimethyl benzenes were found to disappear at rates equal to or exceeding that of ethylene (*4*).

Good evidence for ring fragmentation was found in the rate of decrease in the absorbance of the aromatic carbon hydrogen stretch bands. Aldehydes, peroxyacyl nitrates, and formic acid were identified among the reaction products.

The limited number of measurements which have been made of the eye irritation and plant damage potential of irradiated aromatic hydrocarbon nitrogen oxide systems (*2, 5*) indicate moderately positive effects, but much more extensive data are needed. Knowledge of whether aromatic hydrocarbons are present at significant concentrations in urban atmospheres is essential. In a series of gas chromatographic measurements, the Los Angeles atmosphere was analyzed for benzene, toluene, and the xylenes (*6*). Concentrations of aromatic hydrocarbons in the 0.1 to 0.2 ppm range were found in moderate smogs. Olefins are usually found in these concentrations.

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Australites and Antarctica

Abstract. A meteorite crater in the Wilkes Land region of Antarctica has been postulated as an explanation of the origin of australites. Geophysical data suggest that such a feature may have been located.

It has been suggested recently (*1*) that australites (tektites found in the southern two-thirds of Australia and in Tasmania) may have been splashed from Wilkes Land in eastern Antarctica by the impact of a large meteorite or asteroid. The site of impact was placed in Wilkes Land because this region is most distant from southern South America and South Africa, areas where tektites have never been discovered (*2*).

Eastern Antarctica is a Precambrian shield area, much of which is probably underlain by granite-gneiss (*3*); granite-gneiss crops out on the Adelie Land coast, and seismic evidence suggests its presence at latitude 78°S, longitude 135°E (*4*). Such rock could produce glass of tektite composition if heated to volatilization temperatures (*5*).

A meteorite impact crater may exist beneath the ice of Wilkes Land. Striking gravity minima have been found in the vicinity of 71°S, 140°E (Fig. 1), almost exactly in the place predicted (*1*). A composite gravity profile across the feature shows a negative free air gravity anomaly of about 150 mgal (Fig. 2). In this figure, French values (*6*) have

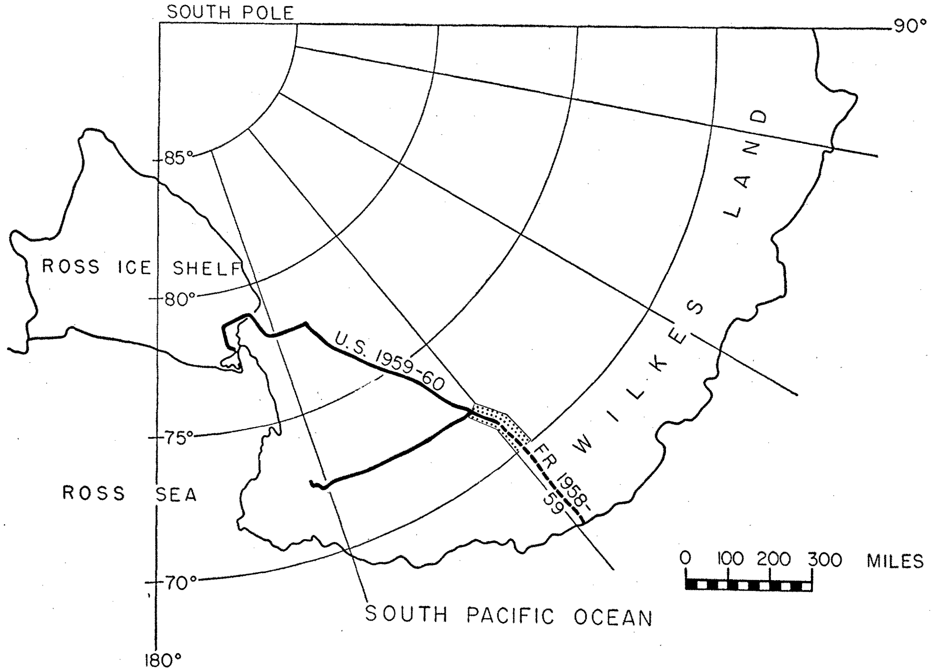

Fig. 1. Australian quadrant of Antarctica, showing location of pronounced gravity minima (stippled). [After American Geographical Society map of Antarctica, 1962]

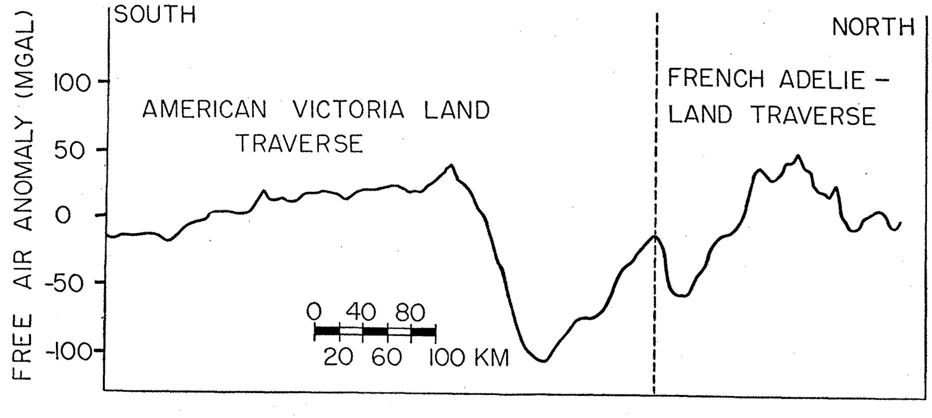

Fig. 2. Free air gravity anomaly profile in the vicinity of 71°S, 140°E. [After Rouillon (*6*) and Weihaupt (*7*)]