height where he can view events with unusual dispassion and wisdom, but I do not understand what he is talking about. The fact is that the Russians, under a cover of soothing assurances, attempted to improve their strategic position; the U.S. did not broadcast its knowledge of the situation until it was in a position to do something about it. It is hard for me to see how this sequence of events can support the conclusion that "duplicity was not confined to one side."—D.S.G.

Photo-oxidation Systems with Added Iodine

Some effects of iodine in dilute photochemical reaction systems containing olefins and oxides of nitrogen in air have been described by Hamilton *et al.* (*1*), who reported that iodine at a concentration of 10 parts per 100 million inhibits or reduces the formation of ozone, and by Stephens *et al.* (*2*), who found that rates of formation of aldehydes and of peroxyacetyl nitrate were materially reduced by iodine at concentrations as low as 25 parts per 100 million. Some experiments in the laboratories of the Air Pollution Control District, County of Los Angeles, have shown that iodine in similar systems may act to accelerate some of the secondary processes, in particular the consumption of nitrogen dioxide and ozone.

These experiments were carried out in a glass chamber of volume more than 1000 cubic feet, illuminated by mercury lamps and fluorescent tubes. Conventional air monitoring instruments were used to record apparent concentrations of nitric oxide, nitrogen dioxide, oxidants, and ozone; concentrations of iodine were calculated from the amounts supplied, and appropriate correction parameters were determined to account for the effects of the iodine on the instruments (especially the oxidant recorder, which depends on the production of triiodide in a column of potassium iodide). With this system (I_2 at concentrations of 25 or 100 parts per 100 million; ozone, olefins, and oxides of nitrogen at slightly higher concentrations) certain facts were demonstrated:

1) In the dark, iodine and ozone react at a moderately rapid rate, strongly dependent on the iodine concentration.

2) In the dark, the rate of reaction between nitrogen dioxide and ozone is substantially increased by the addition of iodine.

3) In the dark, the rate of reaction between olefin (isobutene) and ozone is substantially increased by the addition of iodine.

4) In an irradiated system containing nitric oxide and olefin, the rate of photochemical oxidation of nitric oxide is substantially reduced by the addition of iodine.

5) In the same system, the maximum concentration of nitrogen dioxide reached is essentially unaffected by the addition of iodine.

6) In the same system, the rate of consumption of nitrogen dioxide after the maximum is reached is substantially greater in the presence of iodine.

7) In the same system, the consumption of nitrogen dioxide leads to no accumulation of ozone.

It appears difficult to ascribe these effects of iodine solely to its possible reaction with oxygen atoms produced by the photolysis of nitrogen dioxide. In the system reported by Stephens, 25 parts of I_2 per 100 million (with 5 parts per million each of nitrogen dioxide and *cis*-2-butene) was sufficient to reduce the rate of aldehyde formation to about half the control value. This would imply that at least half the oxygen atoms react with I_2 instead of molecular oxygen, and our calculations suggest that this would require a collision yield of between 3 and 10 for the iodine-oxygen atom reaction.

Perhaps it is more likely that iodine molecules or atoms act specifically to inhibit chain processes in the photochemical system more effectively than do the oxides of nitrogen. Although Stephens *et al.* express doubt that long chains could develop in the presence of oxides of nitrogen, an example of data from the work of Tuesday (*3*) shows that postulation of a long chain is practically unavoidable in some photo-oxidation systems where nitric oxide is the initial reagent, without added nitrogen dioxide. In one case cited by Tuesday, the concentration of nitrogen dioxide was seen to rise from about 2 to 40 parts per 100 million in 2.0 minutes, under irradiation sufficient to decompose nitrogen dioxide in a nitrogen atmosphere at a rate of 0.55 min^{-1}. If the increase in concentration is assumed to be exponential, the rate of increase is 1.5 min^{-1}. This is nearly 3 times the specified nitrogen dioxide decomposition rate and therefore nearly 6 times the rate of primary photolysis, which is also the rate of oxygen atom production. Adding the rate of production of nitric oxide by the primary photolysis

leads to a calculated quantum yield of 6.4 for oxidation of nitric oxide.

In the same experiment, *trans*-2-butene (10 parts per million) was present; this should have reacted with oxygen atoms about 1/25 as fast as the molecular oxygen in the system. If the reaction chains were in fact started by this reaction, the minimum chain yield for oxidation of nitric oxide can be calculated as about 160; if only a fraction of the reactions between butene and oxygen atoms are effective in chain initiation, the chain yield would be even higher. If the chains develop only after those collisions which yield free radicals, the data of Cvetanovic (*4*) suggest that the appropriate factor may be from 3 to 10, giving an estimated chain yield of from 500 to 1600 in the example at hand.

Various investigators have expressed doubt that chains of this order of magnitude can be expected to occur in mixtures containing the odd-molecule oxides of nitrogen, because of the probability that most free radicals would react readily with these oxides. The difficulty is not particularly serious in the case of nitric oxide, inasmuch as the normal products of its reactions with alkoxy or acyloxy radicals would be nitrites, which are readily photolyzed to regenerate the radicals. This is not true of the nitrates, which are produced by reaction of nitrogen dioxide with alkoxy or acyloxy radicals, so there may still exist a legitimate question as to whether chain reactions, particularly long chains, are involved in photo-oxidation when the initial reagent is nitrogen dioxide. Another possibility which may be invoked to account for relatively large chain yields is that chain-branching may occur; thus, a reaction chain of six cycles with a branching factor of 3 would result in a chain yield of 729.

It seems likely that the further study of photo-oxidation systems with added iodine can contribute importantly to unraveling the mechanism of the photochemical smog reaction.

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