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Assessment of the Contribution of Chemical Species to The Eye Irritation Potential of Photochemical Smog

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Eye irritation measurements are available from smog chamber solar irradiations of selected hydrocarbon-nitrogen oxide mixtures. These results have been used to compute eye irritation intensity parameters for formaldehyde, acrolein, peroxyacetyl nitrate, and peroxypropionyl nitrate. Peroxypropionyl nitrate is the most irritating of these four substances. The relative contribution of various pairs of eye irritants in ambient air mixtures to eye irritation has been calculated from the ambient air concentrations and the eye irritation intensity parameters. The relative contribution of the four eye irritants to a "typical" ambient air mixture has been computed. Formaldehyde appears to be the single most significant eye irritant. Other potential ambient air eye irritants are discussed. The relationships between the hydrocarbon control strategies and eye irritation are considered.

Eye irritation has been one of the most aggravating aspects of photochemical air pollution particularly in the Southern California Air Basin. The contribution to eye irritation response of human panelists from chemical species produced in simulated solar radiation of single organics and nitrogen oxides has been the subject of a number of investigations.[1–8] From these studies it has been concluded that neither the hydrocarbon nor nitrogen oxide reactants nor most of the products contribute to eye irritation. The chemical species present in such irradiated systems which contribute to eye irritation are several of the organic vapors formed by the photochemical reactions. It would be desirable to provide for eye irritation potential when modeling alternative control strategies.

Some estimates of eye irritation response parameters have been made from exposures of panelists to the individual eye irritants diluted in air.[2–4] An independent approach is to compute such eye irritation parameters based on the eye irritation response data from panelists during the irradiations of a number of single organic substances mixed with NO_x in air. If a self–consistent set of parameters can be derived by this latter approach, synergistic effects among eye irritants must be unimportant. Use of pollutant mixtures necessitates *a priori* assumption as to the presence of specific sets of eye irritating species.

The eye irritation parameters will be utilized along with analytical measurements of the concentrations of the irritants in atmospheric mixtures to predict the contribution of individual irritants relative to each other in such mixtures. These results can be used to compare eye irritation intensities predicted with those experienced in photochemical smog episodes.

Procedure

An internally consistent procedure would be to use results from the same smog chamber program. Such a program was carried out in a 330 ft^3 chamber with eye irritation exposure panel facilities immediately adjacent in Cincinnati, OH during the 1960's. Use of these measurements insures consistency in the analytical measurement techniques for the pollutants, the same physical facilities with fixed operational characteristics, and the use of consistent exposures of panelists using the same protocols. The results are available in the journal literature.[5–8] Quantification of eye irritation response has involved many variations among the laboratories involved.[1] The eye irritation measurements in Cincinnati were made with groups of panelists exposed to pure dilution air or irradiation mixtures with the order of exposure unknown to panelists. The panel was exposed to the irradiation mixtures only when irradiations under dynamic conditions were near equilibrium or when the products of static experiments leveled off in product concentration. Intensity responses were obtained each 30 seconds and averaged for the panel. The responses used in the computations are corrected for irradiated dilution air responses during the same sets of experiments. All of the results were adjusted to a 0 to 5 intensity scale type response.

Table I. Compositional and eye irritation responses for irradiated organic-nitrogen oxide in air mixtures.

Exp. No.	Organic	Concn. ppm Vol	NO_x Conc. ppm Vol	Concentration of products, ppm Vol Formaldehyde	Acrolein	PAN	PPN	Net eye irritation Index (0–5) Scale	Ref.
1D	Ethylene	3.15	1.0	0.95	0.00	0.0	0.0	1.2	5
2D	Ethylene	6.9	1.0	1.95	0.00	0.0	0.0	1.2	5
3D	1,3-Butadiene	3.3	0.9	0.85	1.0	trace	0.0	3.6	5
4S	Propylene	2.0	0.25	0.85	0.0	0.15	0.0	0.9[a]	6,7
5S	Propylene	2.0	0.5	0.85	0.0	0.27	0.0	1.15	6,7
6S	Propylene	2.0	0.75	0.8	0.0	0.38	0.0	1.35	6,7
7S	Propylene	2.0	1.0	0.8	0.0	0.48	0.0	1.5[a]	6,7
8S	Propylene	2.0	1.5	0.8	0.0	0.58	0.0	1.8	6,7
9S	Acetaldehyde	1.0	0.5	0.3	0.0	0.10	0.0	0.2[a]	8
10S	Acetaldehyde	2.7	0.5	0.5	0.0	0.18	0.0	0.4[a]	8
11S	Acetaldehyde	3.0	1.0	0.28	0.0	0.28	0.0	0.55[a]	8
12S	Acetaldehyde	3.0	1.6	0.78	0.0	0.26	0.0	0.65[a]	8
13S	Propionaldehyde	3.5	0.5	0.17	0.0	0.03	0.13	1.1[a]	8
14S	Propionaldehyde	4.3	0.5	0.3	0.0	0.03	0.13	1.3[a]	8
15S	Propionaldehyde	3.5	1.5	0.3	0.0	0.08	0.22	2.1[a]	8

[a] Duplicate or triplicate runs made at same initial compositions.

Results

The experimental results selected for use to compute eye irritation intensity parameters, are listed in Table I from irradiations of the ethylene-nitrogen oxide, 1,3-butadiene, propylene-nitrogen oxide, acetaldehyde-nitrogen oxide and propionaldehyde-nitrogen oxide systems.[5–8] The average eye irritation intensity parameters computed by solution of simultaneous equations such as $C_{CH_2O}I_{CH_2O} + C_{Acr}I_{Acr} = E.I.$ are listed in Table II. Thus $I_{PPN} > I_{Acr} > I_{PAN} > I_{CH_2O}$ with overall averaged values as follows: Iperoxypropionyl nitrate, 8 ppm^{-1}; Iacrolein, 2.6 ppm^{-1}; Iperoxyacetyl nitrate, 1.5 ppm^{-1}; Iformaldehyde, 0.7 ppm^{-1}. The results taken from these four studies do lead to a reasonably self-consistent set of eye irritation intensity parameters indicating that the assumption of linear additivity for eye irritation effects is acceptable.

Table II. Computation of eye irritation intensity parameters.

Systems	I_{CH_2O}	$I_{acrolein}$	I_{PAN}	I_{PPN}
Ethylene-NO_x	0.9			
1,3-Butadiene-NO_x	0.9	2.6		
Propylene-NO_x	0.7		2.0	
Acetaldehyde-NO_x	0.5		1.2	
Propionaldehyde-NO_x	0.6		1.5	8
Averages	0.7	2.6	1.6	8

The ratios of these parameters are reasonably consistent with those derived from use of single eye irritants in air with panels.[2,3] Schuck and Doyle[2] computed an eye irritation index for acrolein about 2.5 times larger than for formaldehyde. Stephens and co-workers[3] obtained a larger number of positive eye irritation responses from 0.5 or 1 ppm of acrolein than from concentrations of formaldehyde 4 to 5 times higher. The response to PAN was intermediate between that to formaldehyde and to acrolein.[3]

In three atmospheric studies in Los Angeles[9–11] (Table III, Studies 1–3) and in an irradiated auto exhaust investigation[12] (Table III, Study 4) formaldehyde and acrolein were measured. Using the formaldehyde and acrolein concentrations in Table III, along with the eye irritation intensity parameters in Table II for these two irritants, it is estimated from these sets of results listed that acrolein could cause from 35 to 75% as much irritation as formaldehyde and on the average acrolein could cause about half as much irritation as formaldehyde.

Formaldehyde and/or peroxyacetyl nitrate were measured in irradiated atmospheric samples[13,14] (Table III, Studies 5 and 6). The 18 irradiation experiments reported can be divided into two groups (a) 5 experiments with initial hydrocarbon concentrations at or above 10 carbon ppm (b) 13 experiments with hydrocarbon concentrations at or below 5 carbon ppm. The average concentrations measured during these two sets of days are as follows: (a) HC, 12 cppm; NO_x, 0.95 ppm; formaldehyde, 320 ppb; peroxyacetyl nitrate, 45 ppb (b) HC, 3.5 cppm; NO_x, 0.47 ppm; formaldehyde, 160 ppb; peroxyacetyl nitrate, 35 ppb. Applying the eye irritation intensity parameters for formaldehyde and peroxyacetyl nitrate, peroxyacetyl nitrate contributes one-third of the eye irritation contributed by formaldehyde in the higher concentration atmospheric mixtures and one-half of that contributed by formaldehyde in the lower concentration atmospheric mixtures.

Irradiation of auto exhaust from a vehicle without a control device[15] (Study 7) produced sufficient peroxyacetyl nitrate so it should have contributed 90% of the eye irritation associated with formaldehyde. Irradiation of a synthetic 17-component hydrocarbon mixture simulating early morning traffic composition in Los Angeles[16] (Table III, Study 8) produces a peroxyacetyl nitrate concentration which computes to cause 80% of the eye irritation associated with formaldehyde.

The available ambient air analyses of peroxyacetyl nitrate and peroxypropionyl nitrate[17,18] (Table III, Study 9 and 10) result in PAN to PPN ratios of 8 to 1 and 7 to 1. Applying the eye irritation intensity parameters for PAN and PPN, peroxypropionyl nitrate is estimated to contribute 60 to 70% of the eye irritation of peroxyacetyl nitrate.

The smog chamber study[19] of peroxyacyl nitrate yields from a number of regular and premium grade fuels (Table III, Study 11) along with the eye irritation intensity parameters, leads to peroxypropionyl nitrate contributing 110% (regular grade fuels) and 55% (premium grade fuels) of the eye irritation of peroxyacetyl nitrate. Assuming equal usage of the two groups of fuels, peroxypropionyl nitrate contributes on the average 80% of the eye irritation of peroxyacetyl nitrate.

Using averages from the above results it appears that a "typical" ambient air mixture of these eye irritants on a moderately smoggy day *on a relative basis* might be as follows: formaldehyde, 100 ppb; acrolein, 15 ppb; peroxyacetyl nitrate, 20 ppb; peroxypropionyl nitrate, 3 ppb. Multiplying these

Table III. Measurements on eye irritants in atmospheric or smog chamber studies.

Study	Type of Study	Location and Period of Study	Av. Concn. of Eye Irritants, ppb Formaldehyde	Acrolein	PAN	PPN	Ref.
1	Atmospheric samples	Downtown Los Angeles, CA Sept–Nov 1960)	60 ppb	6 ppb	a	a	9
		Pasadena, Calif Sept–Nov 1960	30 ppb	6 ppb	ND	ND	9
2	Atmospheric samples	Downtown Los Angeles, CA Sept–Oct 1961	35 ppb	7 ppb	ND	ND	10
3	Atmospheric samples	Huntington Pk., CA Oct. 1968	66 ppb	6 ppb	ND	ND	11
4	Smog chamber, irrad. auto exhaust: initial conditions 6 cppm; C: NO_x ratios, 12:1 6:1, 3:1	Cincinnati, OH	130 ppb	23 ppb	ND	ND	12
5	Atmospheric samples irrad. in bags transparent to solar radiation	Downtown Los Angeles, CA Oct–Nov. 1967	370 ppb	ND	40 ppb	ND	13
6	Atmospheric samples irrad. in bags transparent to Solar radiation	Downtown Los Angeles, CA Sept–Nov 1968	ND	ND	37 ppb	ND	14
7	Smog chamger, irrad. of auto exhaust, initial conditions 14 cppm C: NO_x ratio 16:1	Cincinnati, OH	440 ppb	ND	170 ppb	ND	15
8	Smog chamber, irrad. of 17 component simulated atm. mixt. initial conditions: 10 cppm, C: NO_x ratio 20:1 solar	Cincinnati, OH	440 ppb	ND	150 ppb	ND	16
9	Atmospheric samples	Riverside, CA	ND	ND	50 ppb	6 ppb	17
10	Atmospheric samples	St. Louis, MO	ND	ND	21 ppb	3 ppb	18
11	Smog chamger, irrad. of auto exhaust C: NO_x ratio 6:1	Bartlesville, OK		ND	95 ppb 90 ppb	18 ppb 10 ppb	19

[a] Measured, but results at or near limits of detectability.

concentrations by the eye irritation intensity factors, and computing the contribution of these four eye irritants on a percentage basis the following percentages result: formaldehyde, 40%; acrolein, 25%; peroxyacetyl nitrate, 20%; peroxypropionyl nitrate, 15%.

Relating Parameters of Eye Irritation to Ambient Response.

Based on the available atmospheric measurements, absolute concentrations three times those of the "typical" mixture above might be expected on quite smoggy days in some parts of the Los Angeles Basin. Applying the eye irritation intensity factors, such a mixture would be computed to cause about 0.5 units of eye irritation in terms of the laboratory eye irritation panel intensity scale used. Such a response would represent perceptible or moderate eye irritation, but does not appear to account for the more severe burning or tearing eye irritation episodes in Los Angeles. The difficulty in duplicating the tearing, burning severe eye irritation effects in the laboratory with realistic concentrations of reactants has been commented on previously.[1] The difficulty in accounting for eye irritation in Los Angeles smog in terms of measured concentrations of known irritants was discussed in early work.[9] The extrapolation of laboratory results on almost any sort of biological testing of limited groups of human subjects (or test animals) to general populations is difficult to accomplish on a quantitative basis.

The possibility of additional atmospheric eye irritants requires discussion. One species reported in irradiated mixtures of benzylic monoalkylbenzenes (toluene, n-propylbenzene, n-butylbenzene, isobutylbenzene, styrene, methylstyrene) with nitrogen oxide is peroxybenzoyl nitrate.[4] The non-benzylic monoalkylbenzenes when similarly irradiated cause little eye irritation. Attempts to detect peroxybenzoylnitrate in the atmosphere in the U. S. and in irradiated auto exhaust mixtures have been unsuccessful.[20–22] Measurement of peroxybenzoyl nitrate in photochemical smog has been reported in the Netherlands using a substantial modification of the original technique.[20,23] Peroxybenzoyl nitrate is of particular interest because of the very high eye irritation intensity reported for this substance.[4]

It is possible to estimate the ambient air concentration to be expected from the laboratory product yield data[4,20] and the ambient air concentrations of benzylic monoalkylbenzenes.[14] Estimates of molar product yields are as follows: toluene, 0.015;[20] ethylbenzene, <0.01;[4,20] n-propylbenzene, 0.01–0.02;[4,20] n-butylbenzene, 0.01;[4] isobutylbenzene, 0.01.[4] The ambient air molar concentrations at the morning traffic peak period in downtown Los Angeles corresponding to a 4 cppm non-methane loading[14] were as follows: toluene, 39 ppb; ethylbenzene, 8 ppb; n-propylbenzene, 2 ppb. The butylbenzenes were not separated sufficiently to estimate separately. No measurable styrene was present.[14] Applying the product yields the estimated yield from the three most abundant benzylic monalkylbenzenes of peroxybenzoyl nitrate would be approximately 0.7 ppb. (The minimum detectable concentration for the original gas chromatography technique used was 2 ppb.) The peroxyacetyl nitrate concentrations reported from solar irradiations of several 4 cppm samples in the same study ranged from 25 to 97 ppb and averaged 50 ppb.[14] Such a low peroxybenzoyl nitrate concentration would be of little concern if it had not been reported that peroxybenzoyl nitrate caused 200 times as much eye irritation as formaldehyde.[4] Relative to peroxyacetyl nitrate (Table II), peroxybenzoyl nitrate would be about 90 times as irritating. Although there is estimated to be 70 times as much peroxyacetyl nitrate present peroxybenzoyl nitrate would still contribute significantly to eye irritation. Relative to the percentage contribution of peroxyacetyl nitrate in the "typical" ambient air mixture, peroxybenzoyl nitrate would increase the predicted eye irritation over that of the other identified irritants by about 25%.

Substituted peroxybenzoyl nitrate compounds have been synthesized from methyl substituted benzaldehydes and styrenes.[24] The contribution of such peroxybenzoyl nitrate compounds to atmospheric eye irritation was estimated not to be significant.[24]

Solar irradiations of olefins measured in the ambient atmosphere such as 1-pentene and 2-methylbutene-1 and 1-hexene result in rapid consumption[2,3,14] with formation of aldehydes as major products.[2,3,24] The aldehydes derived from these olefins can through further reactions produce higher molecular weight peroxyacyl nitrates.[26] A higher observed eye irritation index has been measured for 1-pentene than for any of 11 monoolefins studied.[2] Although these higher molecular weight PAN's have not yet been measured in ambient air systems they may well contribute significantly to the overall eye irritation observed.

Ethyl hydroperoxide a major product of atmospheric photooxidation of propionaldehyde[27] has been reported to have eye irritation potential equal to that of formaldehyde.[28] Propionaldehyde has been shown to be a major product of the photooxidation of such olefins as 1-butene,[5] 2-pentene, 3-hexene.[3] Other alkylhydroperoxides such as methyl hydroperoxide have not been studied as eye irritants but are formed from photooxidation of acetaldehyde,[27,29] an important product of the photooxidation of many olefins.[25]

The atmospheric photooxidation of trichloroethylene has been reported to cause a higher eye irritation level than observed from ethylene or propylene in the presence of nitrogen oxide.[30] Subsequent measurements of the reaction products of photooxidation in the presence of nitrogen oxide indicated dichloroacetyl chloride was a major product with smaller yields of formic acid and phosgene.[31] Dichloroacetyl chloride is reported to be an eye irritant.[32] No formaldehyde, acrolein, or peroxyacyl nitrates were detected.[31]

Laboratory reaction studies with simple mixtures indicate the peroxynitric acid is likely to be a significant product in atmospheric photochemical reactions.[33,34] The structure of peroxynitric acid, $HO_2\,NO_2$ is similar to several other eye irritants so it too may contribute to the intensity of eye irritation observed in ambient atmospheres.

Various investigations have not identified ozone,[1] or sulfur oxide[34,35] as significant eye irritants. Similarly, there are no data indicating that other inorganic substances such as carbon monoxide, nitric acid, or nitrogen dioxide contribute to eye irritation.

Several investigations have included such particulates as diesel oil,[33] crankcase oil,[35] sodium chloride,[35] lamp black,[35] or sulfuric acid,[36,37] formed from sulfur dioxide. The results have indicated no significant association of particulates with eye irritation effects.[1] Removal of all particulate constituents did not cause any reduction in eye irritation in one of these studies.[35] Generation of sulfuric acid from sulfur dioxide did not cause eye irritation.[37] Addition of sulfur dioxide to a number of hydrocarbon-nitrogen oxide systems actually caused a decrease in eye irritation.[36,37] There is some preliminary evidence that organic aerosols may contribute to eye irritation.[37]

Eye Irritation and Control Strategies.

All of the chemical species thus far identified in the laboratory or field as eye irritants are organic vapors. More specifically these species are oxygenated organic vapors including certain aliphatic aldehydes, peroxyacyl nitrates, peroxybenzoyl nitrates. The chloroacetyl chlorides appear to be contributors also as products from certain chlorinated ethylenes. Aliphatic hydroperoxides may also be contributing somewhat to eye irritation. These results suggest that the overall atmospheric effects may be the sum of contributions from a substantial number of organic vapors. It is entirely possible that additional species of somewhat similar chemical structures remain to be identified.

From the standpoint of control strategies it is clear that control of hydrocarbons must reduce eye irritation since the eye irritants are formed from specific hydrocarbons by atmospheric reactions. Smog chamber irradiation studies indicate linear or curvilinear relationships between initial hydrocarbon concentrations and formaldehyde and other aldehydes as reaction products.[12,25] Yields of formaldehyde, acrolein, and other aldehydes are relatively independent of nitrogen oxide concentrations over a wide range of initial concentrations.[6,12,25]

Peroxyacetyl nitrate yields increase curvilinearly with irradiation of increasing concentrations of olefins or aldehydes[6,8] but show more complex behavior with maximum yield similar but not identical to that of ozone as nitrogen oxides concentrations vary in irradiated olefin-nitrogen oxide[6] and alkylbenzene-nitrogen oxide mixtures.[8]

The concentration and distribution of products causing eye irritation formed from the photochemical reactions of various classes of hydrocarbons with nitrogen oxide are such that the eye irritation potentials are in the order: alkylbenzenes > olefins > paraffins > acetylene.[4,8,15] Therefore, reduction of hydrocarbons particularly olefins and alkylbenzenes should lead to concurrent reduction in eye irritants such as formaldehyde, acrolein, and peroxyacyl nitrates. Similar relationships might be expected for other of the related organic vapors indicated as eye irritants.

The formation of specific eye irritants is sensitive to the concentration and proportions of various olefins and alkylbenzenes present in ambient air mixtures. Ozone production occurs more uniformly from a wide range of organics, therefore, changes in concentration and composition should not be expected to have exactly the same effect on eye irritation as on ozone.

Conclusions

1. Eye irritation in the ambient atmosphere or from complex mixtures irradiated in smog chamber is the summed response to a substantial number of organic products particularly oxygenated vapors.
2. There is experimental evidence that inorganic gases or vapors such as carbon monoxide, sulfur dioxide, ozone, or nitrogen oxides do not contribute to eye irritation.
3. There is no experimental evidence that solid particulate matter contributes to eye irritation. However, liquid organic aerosols may possibly contribute to eye irritation.
4. It is likely based on laboratory measurements that several vapors which are eye irritants still remain to be identified in photochemical smog atmospheres.
5. Since hydrocarbon and other organic emissions are the direct precursors to the eye irritants, control of hydrocarbons and other organics must result in significant reductions in eye irritants, although the reductions are not necessarily exactly proportional to the hydrocarbon concentration.
6. The relationships between eye irritant concentration and composition and hydrocarbon concentration and composition are not identical to those between ozone and hydrocarbons. Therefore, reduction in hydrocarbon concentration should not be expected to cause the same amount of reduction for eye irritation intensity as for ozone concentrations.

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