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Reactivities of Exhaust Aldehydes

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Experimental data on smog-forming reactivities of aldehydes were obtained in studies using a photoirradiation chamber. The aldehydes were studied both individually and in mixture typical of mixtures that appear in auto exhaust. Results showed reactivities of the aldehydes to differ greatly. As a group, the aldehydes in exhaust are judged to be as reactive as the olefin group. The aldehyde contribution to exhaust reactivity and methods for assessing such contribution are discussed.

Results from previous studies have shown that, of the organic atmospheric contaminants known to be emitted by automobiles, most hydrocarbons and the aldehydes are smog precursors. Because of the predominance of hydrocarbons in the automobile emission mixture, they were given the earliest and most extensive research attention; as a result, there is a relative abundance of experimental data on the smog-forming reactivity of hydrocarbons.[1] Laboratory evidence on aldehyde reactivity[2,3] is considerably less complete and has not permitted accurate assessment of exhaust aldehydes as smog precursors.

Reactivities of some aldehydes were measured by previous investigators using the smog chamber method.[3] The procedure commonly followed was to irradiate aldehyde in mixture with nitric oxide (NO) and air and measure the resultant smog levels. Results from these measurements were used in conjunction with reactivity scales to assign a reactivity rating to the tested compound.[1] Note that such a rating represents the relative reactivity of that substance when it is exposed individually to atmospheric conditions. There are indications, however, that in a mixture, the mixture's reactivity is not equal to the sum of the contributions surmised for the individual components. This anomaly is commonly referred to as "synergism."[4]

Results from previous Bureau of Mines studies[5] indicated that in irradiated olefin-aldehyde-NO mixtures, formaldehyde synergistically accelerated consumption of the companion olefin, whereas acetaldehyde and propionaldehyde had an inhibitive effect. Although evidence was limited, still the investigators felt justified in assuming that the formaldehyde participation in smog-forming reactions of mixtures may differ in pattern from that of the aliphatic aldehydes as a group.

The present work provides additional data on the reactivity of exhaust aldehydes. The considerations discussed in the preceding paragraphs led to a study, design highlights of which are: (*a*) The aldehyde contribution to exhaust reactivity was measured using test mixtures similar to exhaust at atmospheric dilution; (*b*) the formaldehyde contribution was measured separately from that of the composite of the other exhaust aldehydes.

Experimental

Reactivities of individual aldehydes and of aldehyde/hydrocarbon mixtures were measured in a smog chamber in a series of tests. Mixtures of purified air with organic reactant at 1 ppm and nitrogen oxides (NO_x) at 0.5 ppm [0.44 ppm of NO and 0.06 ppm of nitrogen dioxide (NO_2)] were irradiated. Reactivity was measured and expressed as rate-of-NO_2 formation (R_{NO_2})[6] and yields of reaction products; yields were expressed as maximum levels and dosages, i.e., time integrated levels. The organic reactant was either an exhaustlike mixture of aldehydes and hydrocarbons or an individual component of that mixture.

Exhaustlike mixtures were prepared from the following four blends: (1) Nitrogen with (vaporized) gasoline consisting of 67.6 mole % paraffins, 12.4 mole % olefins, and 20.0 mole % aromatics. (2) Nitrogen with a mixture of ethylene (60.6 mole %), propylene (24.2 mole %), and isobutylene (15.2 mole %). (3) Nitrogen with a mixture of acetaldehyde (50 mole %), butyraldehyde (20 mole %), acrolein (10 mole %), and benzaldehyde (20 mole %). (4) Nitrogen with about 1000 ppm formaldehyde.

Details on the preparation and standardization of these blends have been reported.[7] A measured volume of the gasoline or olefin mixture blend was ininjected into the chamber and resultant total hydrocarbon level was measured with the chamber's flame ionization detector (FID). These measurements provided for each mixture an FID response factor that expressed

the detector response in parts of carbon per part of total hydrocarbon. These response factors and FID data were used to establish initial part-per-million levels of the hydrocarbon mixture reactant in the smog chamber. Initial levels of formaldehyde were established by the chromotropic acid method.[8] Initial levels of the aldehyde mixture were established from the volumes of the aldehyde-mixture blend injected into the chamber. In the individual aldehyde tests, initial levels of aldehydes heavier than formaldehyde were established from FID data assuming the FID response of an aldehyde to be equal to that of the corresponding paraffinic hydrocarbon with one carbon atom less.[9]

Design of and operation procedures for the smog chamber have been described.[6] Subsequent modifications included replacing the Tedlar film windows with Pyrex glass (Corning No. 7740) and adding three 400-watt mercury vapor lamps (GE-H400RST-33-1). These modifications increased chamber light intensity, k_D,[10] from 0.20 to 0.49 min^{-1}. Further, a light monitor[11] was devised and installed on the chamber and light intensity was continuously monitored to detect any large deviation from the average level.

Levels of NO, NO_2, total organic, oxidant, peroxyacetyl nitrate (PAN), peroxybenzoyl nitrate (PBzN), and formaldehyde were monitored throughout the 6-hr irradiation tests by established analytical procedures.[7]

Results

Reactivity data obtained for ten individual aldehydes and three reference hydrocarbons (ethylene, propylene and β-methyl-styrene) are given in Table I. (Experimental data obtained in this study are given in more detail in reference 7.) The reactivity of benzaldehyde was further explored because benzaldehyde may be a precursor of the PBzN eye irritant.[12] Although benzaldehyde alone did not yield PBzN or appreciable levels of oxidant after 6 hr of irradiation, in the presence of other components capable of producing oxidant, benzaldehyde could have reacted to form PBzN. To explore that possibility, a mixture of 0.5 ppm benzaldehyde and 0.5 ppm propylene was irradiated in the presence of 0.5 ppm NO. Additionally, a mixture of 1 ppm β-methyl-styrene and 0.5 ppm NO was irradiated to demonstrate the capability of the analytical system to measure PBzN. Results from this irradiation clearly showed buildup of PBzN to a maximum level of approximately 0.20 ppm. Such level is comparable to that which could be expected on the basis of work by others[12] and validates the PBzN data obtained in this research. Results from the propylene and benzaldehyde tests (Table II) showed that PBzN did form to a maximum of 0.067 ppm.

Table III shows results from chamber tests with the multicomponent mixtures and formaldehyde. For these tests, the organic reactant is expressed as four components, each one being a mixture of fixed composition. These components are: Formaldehyde (HCHO), aldehyde mixture (RCHO), olefin mixture, and (vaporized) gasoline. The olefin mixture and gasoline vapor together are intended to simulate typical exhaust hydrocarbon mixtures. The HCHO and RCHO components together are intended to simulate typical exhaust aldehyde mixtures; however, to assess their reactivity contributions, they were used at levels widely varying and much higher than those found in exhaust.

Mixtures entirely free of HCHO could not be tested in the smog chamber because traces of HCHO were inevitably present in the chamber background air. Such contamination ranged from 0 to 0.07 ppm for most of the tests but 0.2 ppm levels were observed in three of the tests (Table III). To obtain values for individual component reactivity (specific reactivity), the respective measurements were corrected for the contribution of such background HCHO. This contribution was computed by multiplying the mole fraction of background HCHO by the reactivity of HCHO at 1 ppm. Following this HCHO correction, the specific reactivity data were normalized to 1 ppm of organic reactant. This adjustment was made to all except NO_2-dosage reactivities and was made in proportion to the difference between the actual concentration level and the intended level of 1 ppm. Tables I, II, and III show the corrected and normalized reactivities.

Discussion

Reactivity Ratings for Exhaust Aldehydes

The most striking feature of the aldehyde reactivity picture is the extremely wide and nonuniform variation in reactivity characteristics among the members of the aldehyde family (Tables I and IV). For example, HCHO is almost as reactive as propylene (one of the

Table I. Aldehyde and olefin reactivities obtained[a] with smog chamber.

Aldehyde or olefin	R_{NO_2}, ppb/min	Maximum, ppm				Dosage, ppm × min				
		Oxidant	PAN	PBzN	HCHO	NO_2	Oxidant	PAN[b]	PBzN	HCHO
Formaldehyde	8.3	0.18	0.018	—	1.0	80.4	25.7	3.8	—	186
	8.1	0.15	0.013	—	1.0	79.7	22.8	1.9	—	198
	7.6	0.11	0.010	—	1.0	70.4	21.6	1.3	—	190
	8.1	0.12	0.009	—	1.0	68.3	21.9	1.3	—	195
Acetaldehyde	13.6	0.85	0.110	—	0.91	64.7	152	28.6	—	232
	13.7	0.60	0.130	—	0.85	72.4	129	28.6	—	231
	13.3	0.56	0.090	—	0.65	67.0	126	22.5	—	191
Propionaldehyde	23.6	0.63	0.080	—	0.49	56.5	157	15.1	—	100
	21.5	0.64	0.060	—	0.43	57.5	162	12.2	—	99
	22.66	0.62	0.060	—	0.53	54.8	161	11.9	—	124
Butyraldehyde	14.8	0.52	0.030	—	0.51	50.1	130	4.6	—	137
Acrolein	8.39	0.62	0.010	—	0.83	75.0	117	1.8	—	193
	8.81	0.54	0.020	—	0.72	79.4	101	2.6	—	197
Crotonaldehyde	11.5	0.69	0.080	—	0.68	51.0	154	16.7	—	207
	12.6	0.60	0.080	—	0.66	55.8	151	15.8	—	156
Benzaldehyde	1.45	0.01	0	0	0.28	56.7	2.4	0	0	68.0
	1.58	0.04	0	0	0.26	47.0	5.6	0	0	69.6
o-Tolualdehyde	60.6	0.13	0.010	0	0.26	14.4	32.1	3.3	0	51.5
m-Tolualdehyde	2.34	0.07	0.003	0	0.24	60.5	8.4	0.3	0	52.9
p-Tolualdehyde	1.78	0.05	0	0	0.18	60.2	5.0	0	0	47.3
β-Methylstyrene	29.4	0.77	0.130	0.202	1.2	35.9	199	27.5	38.5	340
Ethylene	5.44	0.53	0.025	0	1.2	74.5	103	4.0	0	335
Propylene	9.63	0.75	0.110	0	1.5	43.4	188	28.0	0	422
	9.95	0.63	0.160	0	1.5	36.0	165	37.9	0	398
	10.8	0.66	0.080	0	1.4	48.9	182	23.1	0	382

[a] Obtained by irradiating in the smog chamber mixtures containing 1 ppm of aldehyde or olefin and 0.5 ppm of NO_x.
[b] Only peroxyacetyl nitrate was measured; heavier aliphatic homologues, possibly formed, are not included in reported PAN data.

Table II. Reactivity data for benzaldehyde and propylene.

Reactant	R_{NO_2}, ppb/min	Maximum, ppm				Dosage, ppm × min				
		Oxidant	PAN	PBzN	HCHO	NO_2	Oxidant	PAN[a]	PBzN	HCHO
Propylene,[b] NO_x (1.0, 0.5)[c]	10.1	0.68	0.117	0	1.5	42.8	178	29.7	0	400
Propylene, NO_x (0.5, 0.5)[c]	6.56	0.65	0.110	0	0.94	67.7	125	18.5	0	247
Propylene, Benzaldehyde, NO_x (0.5, 0.5, 0.5)[c]	3.42	0.43	0.050	0.067	0.75	63.2	68	4.9	8.4	173
Benzaldehyde, NO_x (1.0, 0.5)[c]	1.53	0.04	0	0	0.26	47.0	6.0	0	0	70.0

[a] Only peroxyacetyl nitrate was measured; heavier aliphatic homologues, possibly formed, are not included in reported PAN data.
[b] Reactivity values represent averages from three measurements.
[c] Numbers in parentheses represent initial ppm levels of reactants in the smog chamber.

Table III. Reactivities of hydrocarbon, aldehyde, and hydrocarbon-plus-aldehyde mixtures.

Test mixture composition[a]				Reactivity measurement results							
HCHO,[b] ppm	RCHO,[c] ppm	Olefin,[d] ppm	Gasoline,[e] ppm	R_{NO_2}, ppb/min	Oxidant[f] maximum, ppm	PAN max., ppm	HCHO max., ppm	NO_2 dosage, ppm×min	Oxidant[f] dosage, ppm×min	PAN[g] dosage, ppm×min	HCHO dosage, ppm×min
1.00	0	0	0	8.03	0.14	0.012	1.00	74.7	22.9	2.1	192
0	1.00	0	0	8.91	0.42	0.108	0.50	74.5	79.4	22.5	115
0	0	1.00	0	7.88	0.65	0.071	1.21	58.0	144	16.9	320
0	0	0	1.00	7.56	0.43	0.061	0.41	56.2	97	16.1	87
0.10	0	0.20	0.81	8.29	0.46	0.076	0.53	60.3	88	15.2	153
0.13	0	0.20	0.90	8.45	0.54	0.096	0.49	59.8	110	18.1	137
0.09	0.30	0	0.78	8.78	0.51	0.091	0.46	62.4	108	17.7	113
0.09	0.30	0	0.74	8.70	0.54	0.099	0.43	68.1	108	16.9	111
0.11	0.30	0.20	0.56	8.63	0.51	0.099	0.56	62.6	103	20.7	143
0.11	0.30	0.20	0.54	9.01	0.46	0.092	0.52	66.9	93	18.9	163
0.12	0.50	0	0.46	8.24	0.44	0.084	0.42	69.7	74	26.4	122
0.18	0.50	0	0.49	7.77	0.43	0.075	0.49	70.1	80	23.3	137
0.22	0.15	0.20	0.54	9.17	0.51	0.086	0.52	63.9	107	17.6	168
0.25	0.15	0.20	0.55	9.83	0.50	0.079	0.53	65.2	108	15.6	166
0.27	0.15	0	0.78	10.13	0.51	0.076	0.47	63.1	112	16.1	139
0.28	0.15	0	0.74	8.62	0.46	0.079	0.49	69.7	90	15.1	139
0.33	0	0	0.65	9.70	0.50	0.085	0.51	64.3	109	16.5	164
0.34	0	0.20	0.54	8.95	0.43	0.067	0.57	66.6	89	12.9	173
0.40	0	0.20	0.57	9.81	0.55	0.094	0.54	63.9	114	16.4	180
0.42	0	0	0.76	9.18	0.48	0.073	0.46	66.4	97	14.2	147
0.47	0	0	0.78	10.05	0.54	0.073	0.47	62.6	105	13.9	151
0.55	0	0	0.49	9.68	0.42	0.052	0.60	70.2	83	9.9	163
0.58	0	0	0.49	9.65	0.49	0.049	0.58	70.1	84	9.4	175
0.51	0.50	0	0	9.38	0.35	0.060	0.68	78.2	66	11.8	181
0.66	0.50	0	0	9.44	0.35	0.065	0.66	76.6	61	13.2	188

[a] Test mixtures contain hydrocarbons and/or aldehydes at the designated levels and 0.5 ppm NO_x, with NO_2/NO_x at about 0.1.
[b] Reported specific reactivity values represent averages from four measurements.
[c] Mixture of acetaldehyde (50% by vapor vol), butyraldehyde (20%), acrolein (10%), and benzaldehyde (20%). Reported specific reactivity values for the mixture represent averages from two measurements.
[d] Mixture of ethylene (60.6 vol %), propylene (24.2 vol %), and isobutylene (15.2 vol %). Reported specific reactivity values for the mixture represent averages of four measurements.
[e] Gasoline vapors consisting of paraffins (67.6% by vapor vol), olefins (12.4%), and aromatics (20.0%). Reported specific reactivity values for the mixture represent averages from five measurements.
[f] Measured by the neutral KI (1%) method.
[g] Only peroxyacetyl nitrate was measured; heavier aliphatic homologues, possibly formed, are not included in reported PAN data.

moderately reactive exhaust olefins) in terms of R_{NO_2} but considerably less reactive than propylene in terms of maximum oxidant yield. Also, all reactivity manifestations for benzaldehyde and two of the tolualdehyde isomers were practically of zero intensity, whereas the *o*-tolualdehyde showed a surprisingly high level of R_{NO_2} reactivity, higher than that of propylene by a factor of 6. Interestingly, the oxidant yield of *o*-tolualdehyde was lower than that of propylene by a factor of 5.

Such a picture suggests that the main contribution of aldehydes to exhaust reactivity is to promote a rapid photooxidation of NO and early appearance of oxidant. However, the direct contribution of aldehydes to the buildup of smog constituents (such as NO_2, oxidant, PAN, PBzN, and HCHO) should heavily depend on aldehyde composition.

Except for formaldehyde, the saturated aliphatic aldehydes appear to be as reactive in every respect as the olefins. Formaldehyde promoted photooxidation of NO into NO_2 but did not react appreciably with NO_2, neither did it develop high levels of O_3 which would convert NO_2 into N_2O_5 and HNO_3. Such behavior explains the exceptionally high NO_2-dosage reactivity of HCHO.

Except for *o*-tolualdehyde, the aromatic aldehydes were totally unreactive when tested individually. Benzaldehyde in mixture did manifest reactivity in terms of PBzN formation and also it appeared to have reduced the propylene reactivity (see Table II). Although not tested in mixture, the other unreactive aromatic aldehydes (*m*- and *p*-tolualdehyde) are likely also to exhibit such reactivity. Considering the strong eye-irritation properties of PBzN, and presumably of P(Tol)N also, this reactivity of the thought-to-be unreactive aromatic aldehydes cannot be discounted. In fact, judging from other reported studies and from the PBzN data obtained in this study, the benzaldehyde contribution to the eye-irritation reactivity of the propylene/benzaldehyde mixture should be comparable to that expected from a typical reactive aromatic hydrocarbon.[12]

The *o*-tolualdehyde was found to react rapidly during irradiation and to promote rapid photooxidation of NO. While *o*-tolualdehyde was not measured specifically, its rapid disappearance during irradiation was indicated by the decrease of the FID response to total hydrocarbon. The decrease occurred at the average rate of 96% per hour as compared to about 3% per hour for the other aromatic aldehydes.

Concerning the *o*-tolualdehyde reactivity, questions are raised by the un-

usually rapid disappearance of NO_x—causing extremely low NO_2 dosage—that was observed to accompany the tolualdehyde photooxidation process. The NO_x disappearance began immediately after the chamber lights were switched on and continued through the later, ozone-forming reaction phase. The fate of the disappeared NO_x is unknown. Before oxidant appearance, there was no methyl or ethyl nitrate or PBzN formed, and N_2O_5 could not have been present; therefore, these nitrogen-containing products cannot account for reacted NO_x. These uncertainties regarding reaction-product formation must be resolved before the overall reactivity of *o*-tolualdehyde is accurately assessed.

To summarize observations on reactivities of aromatic aldehydes: benzaldehyde, *m*-, and *p*-tolualdehydes were almost unreactive, certainly much less reactive than the corresponding hydrocarbons, toluene, *m*-, and *p*-xylene. Further, benzaldehyde appeared to inhibit reactions of companion hydrocarbon reactants. These observations suggest that with the exception of *o*-substituted aromatic aldehydes, presence of the aldehydic group in the benzene ring has an inhibitive effect on the parent molecule reactant as well as on other hydrocarbon reactants. One possible explanation is that the benzaldehyde group scavenges oxygen atoms, producing benzoyl radicals that do not promote photooxidation of NO into NO_2. However, in the presence of organic reactants (such as propylene) that accelerate photooxidation of NO and formation of ozone, the benzoyl radicals react to form aromatic peroxyacetyl nitrates. The *o*-substituted aldehydes such as *o*-tolualdehyde may owe their high reactivity to the proximity of the carbonyl and methyl groups in the molecular structure. Such proximity could cause interaction between the two ring substituents in the initial molecule or in some intermediate derivative, resulting thus in higher reactivity.

Regarding reactivity of aldehydes in exhaust mixtures, more direct evidence was obtained from the tests with the exhaustlike mixtures (Table III). Reactivity data obtained in these tests were analyzed to show difference in value between measured reactivities and reactivities calculated from composition and specific reactivity data. Results from such analysis are shown in Table V. Specifically, data in Table V represent differences between measured and calculated reactivities of mixtures prepared from gasoline, olefin, RCHO, and HCHO blends at varying proportions. Calculated reactivities were obtained by the linear summation method, i.e., using equation

$$R_{calc} = C_{total}\,[X_{gas.} \cdot r_{gas.} + X_{ol.} \cdot r_{ol.} + X_{RCHO} \cdot r_{RCHO} + X_{HCHO} \cdot r_{HCHO}],$$

where

X = mole fraction
r = specific reactivity for the designated component
C_{total} = total part per million of hydrocarbon and aldehyde in the initial chamber charge

Specific reactivities were measured in the smog chamber with 1 ppm of organic reactant and 0.5 ppm of NO. These specific reactivity values for the gasoline, olefin, RCHO, and HCHO components are included in Table III.

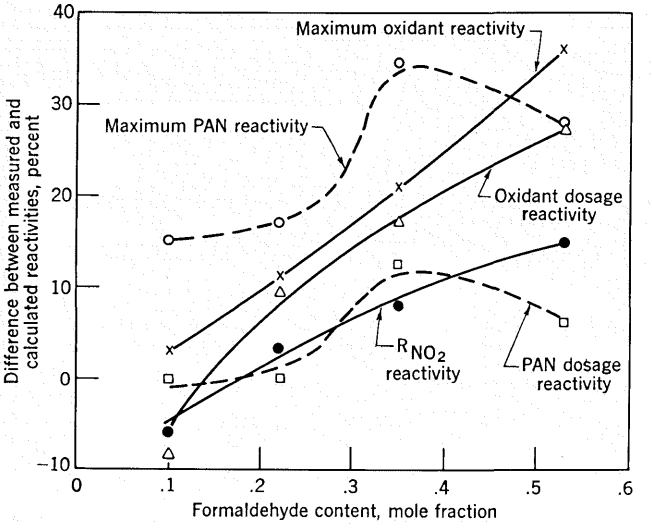

Figure 1. Difference between measured (chamber) and calculated reactivities for hydrocarbon/aldehyde mixtures as a function of formaldehyde content.

The data of Table V show that for the test mixtures with the high relative levels of HCHO ($\geq$22%), measured reactivity values were significantly higher than expected. Furthermore, these differences between measured and calculated reactivity values tended to increase with increasing relative levels of HCHO, as shown in Figure 1. Although the PAN, PAN dosage,

Table IV. Aldehyde reactivities[a] relative to propylene reactivity.

Aldehyde	Reactivity relative to propylene							
	R_{NO_2}	Oxidant max.	PAN max.	HCHO max.	NO_2 dosage	Oxidant dosage	PAN dosage	HCHO dosage
Formaldehyde	0.79	0.21	0.11	0.69	1.7	0.13	0.07	0.48
Acetaldehyde	1.3	1.0	0.94	0.55	1.6	0.76	0.90	0.55
Propionaldehyde	2.2	0.93	0.57	0.33	1.3	0.90	0.44	0.27
Butyraldehyde	1.5	0.76	0.26	0.35	1.2	0.73	0.15	0.34
Acrolein	0.85	0.85	0.13	0.54	1.8	0.61	0.07	0.49
Crotonaldehyde	1.2	0.96	0.68	0.46	1.2	0.86	0.55	0.45
Benzaldehyde	0.15	0.04	0	0.19	1.2	0.02	0	0.17
o-Tolualdehyde	6.0	0.19	0.08	0.18	0.34	0.18	0.11	0.13
m-Tolualdehyde	0.23	0.10	0.02	0.16	1.4	0.05	0.01	0.13
p-Tolualdehyde	0.18	0.07	0	0.12	1.4	0.03	0	0.12

[a] Calculated from data of Table I.

Table V. Differences between measured and calculated[a] reactivities of aldehyde/hydrocarbon mixtures.

Test mixture composition			Number of replicates	Difference between measured and calculated reactivity, %[b]				
Gasoline + olefin[c]	RCHO[d]	HCHO		R_{NO_2}	Oxidant maximum	PAN maximum	Oxidant dosage	PAN dosage
0.90	0	0.10	2	−7.0	−2.3	21.4	−15.6	−5.0
0.65	0.25	0.09	4	−4.9	5.3	15.0	−3.5	−5.0
0.43	0.46	0.11	1	−7.9	4.5	1.2	−17.6	28.4
0.65	0.13	0.22	4	3.2	11.0	16.8	9.4	0
0.65	0	0.35	5	7.9	21.1	34.4	17.1	12.5
0.46	0	0.54	2	14.7	35.9	27.7	27.5	6.1

[a] Calculated by the linear summation method from mole fractions and specific reactivities of mixture components.
[b] Defined as $[(R_{meas.} - R_{calc.})/R_{meas.}] \times 100$.
[c] Designates mixture of gasoline vapors and olefins with exhaustlike composition.
[d] Designates mixture of aldehydes (excluding formaldehyde) with exhaustlike composition.

R_{NO_2}, and oxidant curves of Figure 1 all depict the same directional effect of HCHO, the PAN and PAN-dosage curves differ in configuration, probably because of experimental error.

For the test mixtures with the low relative levels of HCHO ($\leq 11\%$), the data cannot be analyzed meaningfully for HCHO effect because such HCHO levels are comparable to those present in background chamber air. However, the differences in value between measured and calculated reactivities do not seem to relate in any systematic manner to RCHO content in the test mixture. This is interpreted to mean that the heavier aldehydes (RCHO) do not have the enhancing effect on reactivity that formaldehyde has.

Table VI. Reactivity ratings for hydrocarbons[a] and aldehydes typically present in exhaust.

Hydrocarbon or aldehyde	Specific reactivity, scale: 0–10			
	R_{NO_2}	Maximum Oxidant	Maximum PAN	Maximum HCHO
C_1-C_3 paraffins, benzene, and acetylenes	0	0	0	0
$C_{>3}$ paraffins	0.15	3	0	1
Monoalkylbenzenes	0.2	4	1	1
Ethylene	0.3	6	0	8
1-Alkenes	0.6	8	4	10
Diolefins	0.6	7	0	9
Dialkylbenzenes	0.5	6	8	3
Tri- and tetra-Alkylbenzenes	1.0	9	10	7
Internally double-bonded olefins	3.0	9	10	8
Formaldehyde	0.5	2	0	8
Aliphatic $C_{>1}$ aldehydes	0.9	9	6	5
Benzaldehyde and m- and p-tolualdehyde	0	0	0	1
o-Tolualdehyde	3.5	2	0	1

[a] Values for hydrocarbons were derived from data reported in reference 12.

Table VII. Composition[a] and reactivity data for typical exhaust.

Exhaust component	Mole Fraction	Reactivity contribution[b]			
		R_{NO_2}	Maximum oxidant	Maximum PAN	Maximum HCHO
C_1-C_3 paraffins, benzene, and acetylenes	0.24	0	0	0	0
$C_{>3}$ paraffins	0.21	0.032	0.63	0	0.21
Ethylene	0.15	0.045	0.90	0	1.20
1-Alkenes	0.12	0.072	0.96	0.48	1.20
Internal olefins	0.025	0.075	0.23	0.25	0.20
Diolefins	0.020	0.012	0.14	0	0.18
Monoalkylbenzenes	0.10	0.020	0.40	0.10	0.10
Dialkylbenzenes	0.020	0.010	0.12	0.16	0.06
Tri- and tetra-Alkylbenzenes	0.025	0.025	0.225	0.25	0.18
Aldehydes	0.091	0.057	0.37	0.17	0.60
Formaldehyde	0.0545	0.027	0.11	0	0.44
Aliphatic $C_{>1}$ aldehydes	0.0291	0.026	0.26	0.17	0.15
Benzaldehyde and m- and p-tolualdehyde	0.0064	0	0	0	0.006
o-Tolualdehyde	0.0010	0.004	0.002	0	0.001
Total	1.00	0.348	3.98	1.41	4.36
(Aldehydes/total) × 100	9.0	16.4	9.3	12.1	13.8
(Aldehydes/hydrocarbons) × 100	10.0	19.6	10.2	13.7	16.0

[a] Hydrocarbon composition data were obtained from analyses of exhaust from eight 1968 automobiles and one fuel (prototype API No. 1).[16] Total aldehyde level was assumed to be 10 mole % of that of total hydrocarbon; aldehyde composition was taken to be similar to that reported in the literature.[15]

[b] Obtained by multiplying mole fraction by specific reactivity in 0-to-10 scale (see Table VI).

The reactivity data obtained in this study were used to give reactivity ratings to aldehydes analogous to those given to hydrocarbons.[1] Such hydrocarbon and aldehyde ratings on a 0 to 10 scale are given in Table VI for four reactivity manifestations: R_{NO_2}, yields of maximum oxidant, maximum PAN, and maximum HCHO.

Contribution of Aldehydes to Exhaust Reactivity

While these results establish unequivocally that exhaust aldehydes as a group are reactive, the actual aldehyde contribution to exhaust reactivity depends on the aldehyde concentration level relative to the hydrocarbon level. Furthermore, any estimate of such contribution depends also on the method of reactivity measurement.

Information on relative levels of aldehydes and hydrocarbons in exhaust is scarce and of questionable reliability. From several hundreds of tests performed by the Bureau using pre-1970 automobiles and fuels, aldehyde levels in exhaust—as measured by the MBTH method[13]—were found to range from 0.05 to 0.07 mole of total aldehyde (as HCHO) per mole of total hydrocarbon. After correction for the MBTH-response error,[7] these mole fraction values become 0.06 to 0.09. In other studies[14,15] where the 2,4-dinitrophenylhydrazone method was used, reported values for aldehyde to total hydrocarbon ratio in exhaust ranged from 0.07 to 0.35[14] and from 0.12 to 0.20.[15] Analysis of this information[7] led these investigators to conclude that total aldehyde level in exhaust from pre-1970 autos is about 10% of that of total hydrocarbon on a molar basis and about 5% on a carbon atom basis.

Reported data on detailed composition of exhaust aldehydes are scarce and suggest wide variation.[15] An evaluation of these data provided the following typical composition of exhaust aldehydes in mole %.

Formaldehyde	60
Aliphatic $C_{>1}$ aldehydes	32
Benzaldehyde	5
Aromatic $C_{>7}$ aldehydes	3

The aromatic $C_{>7}$ aldehydes can be assumed reasonably to consist of the three tolualdehyde isomers at the same relative proportion as those of the three xylene isomers in typical gasoline fuels, namely, 3:2:5 for the *o*-, *m*-, and *p*-isomers, respectively.

Using the aldehyde level and compositional data given above and the specific reactivity data of Table VI, calculations were made of the reactivity contribution of aldehydes in typical exhaust. Results are given in Table VII.

Use of the reactivity ratings of Table VI to estimate aldehyde contribution

to exhaust reactivity should be made with recognition of the uncertainties inherent to this estimation method. For example, relative reactivity manifestations are not constant but depend to some extent on the organic-to-NO_x ratio. Also, aromatic aldehydes were given zero ratings for PAN reactivity because of their failure to produce PAN when tested individually; however, in mixture, they may react and yield significant levels of aromatic PAN compounds.

Conclusions

In terms of chemical smog manifestation, exhaust aldehydes as a group should be classified among the reactive exhaust components. Specific reactivity of HCHO, as measured by R_{NO_2} formation, is comparable to that of the average exhaust olefin. However, in terms of oxidant yield, HCHO specific reactivity is considerably lower than that of the average exhaust hydrocarbon. Specific reactivity of the heavier aldehyde group is in every respect comparable to that of the average exhaust olefin.

When tested individually, benzaldehyde, *m*-tolualdehyde, and *p*-tolualdehyde are totally unreactive; *o*-tolualdehyde is reactive. In mixtures, benzaldehyde and presumably all aromatic aldehydes manifest reactivity as precursors of the strong eye irritants, aromatic peroxyacyl nitrates.

Mixtures containing HCHO appear to possess higher oxidant yield reactivity than that expected from the specific reactivity and compositional data; the difference increases with increasing HCHO content.

As calculated, the contribution of aldehydes to R_{NO_2} reactivity of typical exhaust is 16.4% of total exhaust reactivity; contributions to oxidant and formaldehyde yields are 9.3% and 13.8%, respectively.

An evident implication of these findings is that methods for exhaust reactivity assessment based on FID measurement are expected to yield erroneously low reactivity values because they fail to include the entire HCHO contribution and part of the heavier aldehyde contribution.

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