

Carbonyl Formation from Isooctane Combustion in an Internal Combustion Engine

ROBERT F. HILL

Research Laboratories, General Motors Corporation, Warren, Michigan 48090

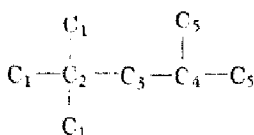
and

S. S. PENNER

University of California, San Diego, LaJolla, California 92037

Experimental measurements of reaction intermediates formed in hydrocarbon oxidation have been performed in laboratory [1, 2] and engine studies [3, 4]. In particular, labeled 2-methylpentane has been used to study the formation and origin of ketones [5]. Mayer and Krause [6] conducted experiments with carbon-14 labeled isooctane in a single-cylinder engine.¹ In this paper we correlate carbon atoms in the fuel molecule with carbonyl compounds separated from the exhaust gas. The "tendency" for carbon-carbon bond rupture and a "measure" of the probability of carbonyl-compound formation are derived.

Isooctane 5-C¹⁴ and 4-C¹⁴ were used [6]. The carbon skeleton is shown below.



The isooctane was fed directly into the intake manifold of a single-cylinder engine. The carbonyl compounds in the exhaust gas were extracted with

cold 2,4-dinitrophenylhydrazine. The resulting hydrazone derivatives were dissolved and separated by paper chromatography, measured by spectrophotometry, and analyzed for carbon-14 content by liquid-scintillation spectrometry. Six experiments were performed (three with 5-C¹⁴ and three with 4-C¹⁴). Approximately 55 liters of exhaust gas were processed in each test. The carbonyl compounds averaged 8.4×10^{-7} mole/liter of exhaust gas, which is equivalent to about 37 ppm.

The following carbonyl compounds were identified: formaldehyde (group 1), acetaldehyde (group 2), and acetone (group 3) separated as individual compounds; propionaldehyde and acrolein (group 4) were separated together; the four carbon-chain compounds also separated as a group and contained the butyraldehyde isomers and crotonaldehyde (group 5). A small quantity of six and seven-membered ketones was also collected (group 6). The results are listed in Table 1.

In the following scheme of data interpretation, we describe the observational data by a procedure that cannot answer the question of location of initial attack but rather shows the final effects of hydrogen abstraction, oxidation and bond rupture on the resulting collection of decomposition fragments.

Let T_{ij} equal the tendency for the carbon bond $C_j - C_j'$ to break during an event and let R_k

¹ This report may be obtained through a request to the General Motors Research Laboratories, Warren, Michigan 48090.

TABLE 1
Specific Activity of Carbonyl Compounds
Formed in a Fired Engine [6]

Group "k"	Concentrations mole %	Specific activity, $\mu\text{Ci}/\text{mole}$	
		3-carbon tagged	4-carbon tagged
1	64.0	24.3	20.7
2	5.4	49.9	153.0
3	5.9	28.8	48.7
4	5.6	62.9	134.0
5	17.7	73.9	113.0
6	1.4	123.0	183.0
	100.0		

represent a *measure* of the fact that the resulting structures were oxidized to the carbonyl compounds of group "k". The activity of the carbonyl compounds of group "k" containing labeled-carbon atom "i" is defined as $kA_i = kS_i M_k$, where kS_i equals the specific activity of "k" associated with carbon atom "i" and M_k equals the mole fraction of "k" formed. Setting the measured activity of the carbonyl compounds in a specified group equal to the sum of the products of the tendencies (T_{ij}) and measures (R_k) that may lead to their formation from iso-octane results in the set of equations listed in Table 2. The numerical values refer to *measured amounts* and the subscripts "k" correspond to the group indices of Table 1.

TABLE 2
Formation of Carbonyl Compounds in Group "k"
with Carbon Atoms 4 and 5

$1A_5 = 15.5 = T_{45} R_1$	
$1A_4 = 13.2 = T_{34} T_{45}^2 R_1$	
$2A_5 = 2.7 = T_{34} T_{45} R_2$	
$2A_4 = 8.5 = (2T_{34} T_{45} + T_{23} T_{45}^2) R_2$	
$3A_5 = 1.7 = (T_{16} + T_{15} T_{45}) R_3$	(a)
$3A_4 = 2.9 = (T_{16} + 2T_{15} T_{45} + T_{12} T_{45}^2) R_3$	(b)
$4A_5 = 3.5 = (T_{16} + T_{15} T_{45}) R_4$	
$4A_4 = 7.5 = (T_{16} + 2T_{15} T_{45} + T_{12} T_{45}^2) R_4$	
$5A_5 = 13.1 = (T_{15} + T_{12} T_{45}) R_5$	
$5A_4 = 20.0 = (T_{15} + 2T_{12} T_{45}) R_5$	
$6A_5 = 1.7 = (3T_{12} T_1 + 3T_{12}^2) R_6$	
$6A_4 = 2.6 = (T_{12}^2 + 6T_{12} T_{15} + 3T_{12}^2) R_6$	

Reference to Table 2 shows that we have a system of 12 equations in 10 unknowns (R_1 through R_6 and T_{12} , T_{23} , T_{34} and T_{45}). Solutions to this overdetermined set are listed in Table 3; the duplicate entries for R_3 refer to the use of the relations identified as (a) and (b), respectively, in Table 2. Perhaps the variation in R_3 from 0.67 to 0.83 is observed because acetone formation occurs not only as the result of simple bond rupture and oxidation, as assumed in our model, but also as the result of synthesis from smaller fragments; in any event, the observed variation is within the experimental limits of error.

The tendency for the carbon bond C_2-C_3 to rupture more readily than C_3-C_4 (1.22 and 0.99, respectively) is a result of the observed formation of large concentrations of the butyraldehydes shown by the value 17.7 for the compounds in group 5 (Table 1). More generally, the data listed in Table 3 provide relative estimates for the tendencies for bond rupture ($T_{23}/T_{12} \sim 1$, $T_{34}/T_{12} \sim 0.83$, $T_{45}/T_{12} \sim 0.72$) during iso-octane combustion in an engine. This tendency for bond rupture varies by a factor of 1.4 which is in general agreement with Pauling's data on bond-dissociation energies in polyatomic molecules [7]. The measure of carbonyl-compound formation varied by a factor of 78 with formaldehyde being the most abundant. Relative measures may be interpreted as indicated ease of aldehyde or ketone formation for the carbon-chain fragments ($R_2/R_1 \sim 0.18$, $R_3/R_1 \sim 0.04$, $R_4/R_1 \sim 0.10$, $R_5/R_1 \sim 0.27$, $R_6/R_1 \sim 0.01$). If we assume formation of negligibly small amounts of acrolein compared with propionaldehyde, we must conclude that aldehyde formation for the three-

TABLE 3
Values of T_{ij} and R_k that Satisfy the
Equations in Table 2

$T_{12} = 1.22$	$R_1 = 18.0$
$T_{23} = 0.99$	$R_2 = 3.18$
$T_{34} = 0.86$	$R_3 = 0.83; 0.67$
	$R_4 = 1.72$
	$R_5 = 4.81$
	$R_6 = 0.23$

carbon chain is about twice as likely to occur as ketone formation, a not unreasonable conclusion for the extreme conditions in engine combustion since there are two end carbon atoms that can result in aldehyde formation while only the middle carbon atom can contribute to ketone formation.

References

1. Tipper, C. F. H., *Oxidation and Combustion Reviews*, Vol. 1, American Elsevier, New York (1965).
2. Barat, P., Cullis, C. F., and Pollard, R. T., The cool-flame oxidation of 3-ethylpentane, *Proc. Roy. Soc. (London) A* **325**, 469 (1971).
3. Ninomiya, J. S., and Golovoy, A., Effects of air-fuel ratio on composition of hydrocarbon exhaust from isooctane, diisobutylene, toluene, and toluene-n-heptane mixture, *SAE Paper 690504* (1969).
4. Fleming, R. D., and Eccleston, D. B., The effect of fuel composition, equivalence ratio, and mixture temperature on exhaust emissions, *SAE Paper 710012* (1971).
5. Cullis, C. F., Hardy, F. R. F., and Turner, D. W., The point of oxygen attack in the combustion of hydrocarbons II. The formation and origin of ketones, *Proc. Roy. Soc. (London) A* **251**, 265 (1959).
6. Mayer, W. J., and Krause, D. P., Oxidation of isooctane in spark ignition engine combustion, *GMR Report 1182*, General Motors Research Laboratories, Warren, Mich. (1972).
7. Pauling, L., *The Nature of the Chemical Bond* Cornell U.P., New York (1960).

(Received June 1972; revised version received August 1972)

MEETING REPORT

Fourteenth Symposium (International) on Combustion

The Fourteenth Symposium (International) on Combustion was held August 20-24, 1972, on the campus of The Pennsylvania State University, University Park, Pa. Final registration totals included 701 registrants from 25 countries, plus 222 wives and children. The technical program included the plenary lecture by Professor Hoyt C. Hottel of M.I.T. on "Combustion and Energy for the Future" and 27 sessions of technical papers that included 12 invited reviews and 121 contributed papers. Four colloquia were organized for the meeting: "Elementary Reactions in Combustion" (37 papers), "Flames in Furnaces and Combustors" (11 papers), "Pollutant Formation and Destruction in Flames" (27 papers), and "Fire and Explosion" (21 papers). Other sessions were held on Laminar Flames, Oxidation and Ignition, Oscillatory Combustion, Turbulent and Supersonic Combustion, Detonations, Propellant Research, and Heterogeneous Combustion. Papers were generally excellent and a great deal of lively and

fruitful discussion took place at sessions throughout the week. The full proceedings will be published by the Combustion Institute during 1973. Orders can be placed by writing to the Executive Secretary, Mrs. Helen G. Barnes, The Combustion Institute, Union Trust Building, Pittsburgh, Pa. 15219.

Nontechnical activities associated with the meeting included tours of the Central Pennsylvania countryside for overseas visitors on August 19, a welcoming reception on the 20th, a string quartet concert on the 21st, a theater party on the 22nd, a picnic and cave trip on the 23rd, and the Institute Banquet on the 24th. An extensive Ladies Program included a variety of expeditions, special programs, teas, and luncheons.

At the Banquet, Combustion Institute awards were presented as follows:

The Sir Alfred Edgerton Medal "for distinguished continuing and encouraging contributions to the field of combustion" to Dr. William