phenomenon was observed with trimethylphenylammonium iodide, the SIMS spectrum of which showed the intact cation *m/z* 136 (52% relative abundance) and fragments due to loss of $CH_3\cdot$ (121^+, 22%), CH_4 (120^+, 30), $2CH_4$ (104^+, 10), C_6H_6 (58^+, 100) and $CH_4 + C_6H_6$ (42^+, 70). However, when this salt was mixed with approximately equimolar amounts of KF, KCl, KBr, and KI, the major ions observed were the series $C_6H_5F^{+\cdot}$, $C_6H_5Cl^{+\cdot}$, $C_6H_5Br^{+\cdot}$, and $C_6H_5I^{+\cdot}$. The fragment ion $C_6H_5^+$ was also present. Reversal of the quaternization reaction accounts for $C_6H_5X^{+\cdot}$ formation, although its observation as a charged species was unexpected given that trimethylamine has the lower ionization energy. Tetraphenylarsonium chloride mixed with the potassium salts of the halides showed exactly analogous results.

To further test the potential of this methodology, several compounds of biological significance were examined. Choline chloride was selected for comparison with the results of desorption from a field desorption emitter in a chemical ionization source.[9] The spectrum (Figure 2) shows the intact cation together with fragment ions due to the expected elimination of an alkane or substituted alkane molecule, in this case CH_4 and CH_3CH_2OH. The field emitter procedure gave similar results,[9] although an ion at *m/z* 90 due to dealkylation and protonation of choline was seen in this latter experiment.

The possibility of observing organic dications in SIMS was of interest, although the absence of these ions in gas-phase chelation[10] must be noted. The diquaternary *N,N'*-dimethyl-4,4'-bipyridyl dichloride did not yield an observable dication in SIMS but showed an ion at *m/z* 171 which corresponds to methyl cation loss from the dication.

Traditionally, involatile and unstable compounds have been derivatized for mass spectrometry by forming volatile and often less polar compounds. To study gas-phase ions from such involatile compounds, it may be advantageous to employ SIMS and start with fully ionized species in the solid phase.

Acknowledgment. This work was supported by the National Science Foundation CHE 77-01295 and NSF-MRL DMR 76-00889A1.

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(5) Instrument parameters and sample preparation processes for SIMS have been described.[6] In all cases the organic was physically mixed with the metal salt and burnished onto Pt foil. A 5-keV Ar^+ primary ion beam of 1-5 $\times 10^{-9}$ A was used to bombard the sample. The mass-analyzed primary ion beam is deflected 3° to eliminate neutrals before entering the ultra-high-vacuum bell jar and striking the sample at ~45° to the target normal. Secondary ions pass through an energy prefilter and are mass analyzed in a quadrupole mass analyzer.
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Reactions in Dry Media. Cleavage of Carbon-Carbon Single Bonds by Ozonation

Sir:

Ozonation of compounds adsorbed on silica gel has recently become a method of general applicability for the hydroxylation of tertiary C-H bonds in saturated compounds.[1-4]

We have recently observed that ozone cleaves not only C-H bonds but also $C-CH_3$ bonds. Thus dry ozonation of *trans*-1,4-dimethylcyclohexane gave in addition to *trans*-1,4-dimethylcyclohexanol small amounts of 2,5-dimethylcyclohexanones and 4-methylcyclohexanone.[5] Similar cleavage of $C-CH_3$ bonds was observed in ozonation of 3,7-dimethyloctyl acetate by Beckwith et al.[3a]

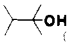
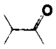
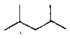
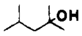
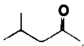
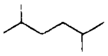
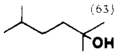
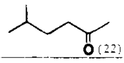
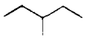
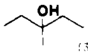
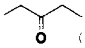
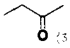
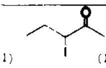
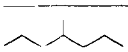
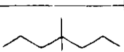
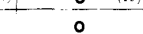
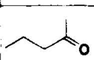
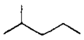
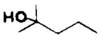
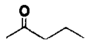
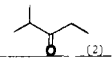
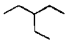
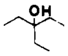
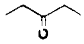
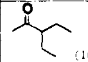
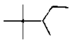
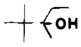
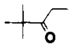
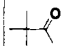
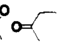
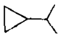
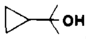
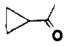
We report here on dry ozonations carried out on a number of aliphatic hydrocarbons (Table I), the results of which show that a substantial cleavage of C-C bonds occurs, caused by a direct insertion of ozone into these bonds.

The reactions were carried out by adsorbing the substrates on silica gel (1%), passing through it a stream of ozone (3% in oxygen) for ~2 h at −45 °C, and then removing the excess of ozone by a stream of argon at the same temperature.[1b,e]

The total yield of the neutral ozonation products was in all cases between 80 and 90%.[6] However, the relative yields of the tertiary alcohols were considerably lower than those obtained on the ozonation of cyclic hydrocarbons, as comparatively large amounts of ketones, originating from the cleavage of alkyl groups, were formed (Table I).

The oxidation of these aliphatic hydrocarbons is a relatively slow process,[7] resulting in constant product ratios throughout the reaction. Thus, 3-methylpentane (Table I, entry 4) was converted after 10 min in 15% yield and after 2 h in 85% yield to the same mixture of an alcohol and ketones. The most significant results emerging from these ozonation data (Table I) are that the ratios of ketones formed by the cleavage of either primary, secondary, or tertiary alkyl groups are in the same order of magnitude and not substantially different. This is best exemplified by a 2:1:1.5 ratio of the ketones formed by the cleavage of methyl, ethyl, and *tert*-butyl groups in 2,2,3-trimethylpentane (Table I, entry 8).

Table I. Product Distribution from Ozonation of Some Hydrocarbons[a] at −45°C

Entry	Starting Material	Product Distribution (molar yield[b], %)		
1		 (35)	 (28)	 (37)
2		 (43)	 (38)[c]	 (19)
3		 (63)	 (22)	 (15)
4		 (34)	 (19)	 (31)  (16)
5		 (30)	 (19)	 (51)
6		 (21)	 (25)	 (52)  (2)
7		 (48)	 (42)	 (10)
8		 (48)	 (20)	 (10)  (14)  (8)
9		 (57)	 (37)	 (6)

[a] The substrates were preadsorbed on silica gel (1% w/w). [b] Based on detected products by VPC analysis. [c] Included small amounts of diisopropyl ketone.

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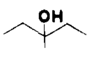
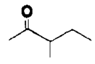
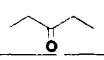
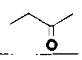
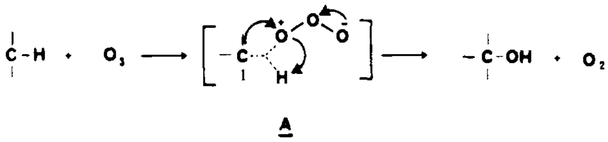
Table II. Product Distribution[a] from Ozonation of 3-Methylpentane at Various Temperatures

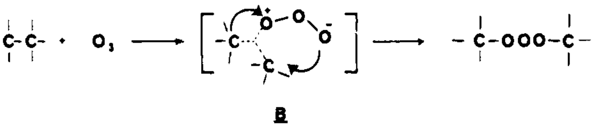
Temp. (°C)				
-45	32	15	20	33
-23	30	15	20	35
0	22	13	20	44
30	8	10	23	60

[a] In molar yield (percent), and based on detected products by VPC analysis.

Scheme I



Scheme II



However, when the ozonation temperature is raised above −20 °C, the respective amounts of the ketones originating from the cleavage of the more highly substituted alkyl groups increases mainly at the expense of the tertiary alcohols as shown by the products distribution in 3-methylpentane at various temperatures (Table II). This temperature dependence is even more pronounced in 2,3-dimethylbutane which at 25 °C gives 70% acetone and 1.5% 2,3-dimethylbutan-2-ol compared with 27% and 31% respectively at −45 °C (Table I, entry 1).

Thus it may be assumed that at higher temperatures the fragmentation of alkanes into ketones occurs mainly via tertiary alkoxy radicals generated in the initial cleavage of the tertiary C–H bonds by ozone.[8]

On the other hand, the product distribution at low temperatures indicates that the fragmentation of the C–C bonds cannot result solely from the attack of ozone on the tertiary C–H bonds.[9] Neither is the formation of the cleavage products by an attack on the primary or the secondary C–H bonds probable. Ozonation of the secondary C–H bonds leads to ketones which are stable under these experimental conditions. The reactivity toward ozone of the primary C–H bonds is comparatively low (the relative activity toward ozone of primary to secondary and tertiary hydrogens was estimated to be ~0.01:0.1:1[10]) and, if products are formed, they will be mainly the corresponding carboxylic acids and to a lesser degree the primary alcohols, but not C–C fragmentation products.

We therefore assume that an alternative mechanism involving a direct insertion of ozone into C–C bonds operates. This insertion leads to the highly reactive dialkyl trioxides which decompose to give the cleavage products.[11] The formation of acetone as a product of ozonation of 2,2,3-trimethylpentane (Table I, entry 8) may be explained by this mechanism. To gain additional evidence for the direct attack of ozone on the C–C bond, we have chosen to ozonize neopentane and have isolated 8% acetone as the only product.[12]

We have previously proposed that the mechanism of C–H bond ozonation involves the formation of an ozone-alkane complex[13] which decomposes electrophilically inserting an oxygen atom into the C–H bond. The transition state for this reaction may be represented by a dipolar structure A (Scheme I) containing a pentacoordinated carbon atom analogous to that proposed by Olah for ozonations of alkanes in superacids,[14] decomposing with the evolution of a molecule of oxygen. We assume that the reaction of the neutral ozone with the C–C bonds proceeds also by a mechanism similar to that considered by Olah for the analogous reaction of protonated ozone,[15] namely through a dipolar intermediate B (Scheme II), which collapses forming dialkyl trioxide.

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(3) (a) A. L. J. Beckwith, C. L. Bodkin, and T. Duong, *Aust. J. Chem.*, **30**, 2177 (1977); *Chem. Lett.*, 425 (1977). (b) A. L. J. Beckwith and T. Duong, *J. Chem. Soc., Chem. Commun.*, 413 (1978).

(4) (a) This method is less favorable for the oxidation of secondary C–H bonds, except in special cases, such as in case of bonds in vicinal position to a cyclopropyl group.[4b] (b) E. Proksh and A. de Meijere, *Angew. Chem., Int. Ed. Engl.*, **15**, 761 (1976); *Tetrahedron Lett.*, 4851 (1976).

(5) Reference 1b and unpublished results.

(6) When the ozonation was performed either in neat or in CCl_2F_2 solution, the conversions were much lower, but the products distribution was similar to that of dry silica. Thus, after 2-h ozonation of a solution of 3-methylpentane at −45 °C, the total yield was 6% products which consisted of methyl ethyl ketone, diethyl ketone, 3-methylpentan-2-one, and 3-hydroxy-3-methylpentane in a 2:1:2:5 ratio.

(7) As compared to the ozonation of olefins or amines which are very fast reacting under similar conditions.

(8) A free-radical mechanism was postulated for ozonation of hydrocarbons at temperatures of 10–40 °C: L. V. Ruban, S. K. Rakovski, and A. A. Popov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **9**, 1950 (1976).

(9) Ozonation of tertiary alcohols at −45 °C results in low conversion to a mixture of ketones, with a preponderance of the ones originating from the cleavage of the more substituted C–C bonds. This is exemplified by the formation of acetone and methyl propyl ketone in 9:1 ratio and 3% total yield from ozonation of 2-hydroxy-2-methylpentane.

(10) G. R. Hamilton, B. S. Ribner, and T. M. Hellman, *Adv. Chem. Ser.*, **No. 77**, 15 (1968).

(11) The formation of a trioxide was postulated previously by T. Preuss, E. Proksch, and A. de Meijere, *Tetrahedron Lett.*, 833 (1978), to explain the cleavage of the C–C bond in bicyclo[*n*.1.0]alkanes as well as by Beckwith et al.[3a] for the formation of ketones from 3,7-dimethyloctyl acetate and saturated derivative of cyclopentadiene trimer.

(12) The formation of acetone by a mechanism involving oxidation of the methyl group is unlikely. The ozonation of the corresponding primary alcohol, the neopentyl alcohol, under similar conditions gave as a major product pivalic acid and undetectable amounts of acetone.

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Received July 25, 1978

Organometallic Models for Possible Fischer–Tropsch Intermediates. Synthesis, Structure, and Reactions of a Formaldehyde Complex of Osmium

Sir:

The interrelationship between organometallic chemistry, surface chemistry, and heterogeneous catalysis has been discussed by several authors.[1] A recognized role for organometallic chemistry is to provide stable models for postulated surface species thus allowing structural studies to define precisely the geometrical features of the interaction between ligand (postulated as intermediate) and transition metal atom. For the Fischer–Tropsch reaction, various mechanisms have been considered[2] and in a recent review Henrici-Olivé and Olivé put forward[3] a plausible scheme which involves successive formation of formyl, formaldehyde, hydroxymethyl, carbene, and alkyl surface intermediates. Now that several transition metal formyl derivatives have been characterized,[4] each of these bound intermediates is firmly grounded upon

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