duced the rate constant for the unimolecular decomposition (eq. 1) to be: $k_1 = 1.7 \times 10^{18} \exp(-94,400/$ RT) sec.⁻¹ with an estimated uncertainty of ± 4 kcal./mole.¹⁴ If we accept an activation energy of 1 to 2 kcal./mole for the recombination of CF3 radicals,^{15,16} then $D(CF_3-CF_3) \approx 93 \pm 4$ kcal./mole and with $\Delta H_f(C_2F_6) = -303$ kcal./mole we find $\Delta H_{\rm f}({\rm CF}_3) = -105 \pm 2 \, {\rm kcal./mole.}$ These results, together with all previous investigations, are summarized in Table I. Our results are in agreement with the value deduced by Corbett, Tarr, and Whittle, which was based, however, on their unusually high C-H bond energy in CF_3H . The above value for the heat of formation of CF_3 , when used with the now relatively well established $D(CF_3-H) = 102$ kcal./mole, leads to $\Delta H_{\rm f}({\rm CF_3H}) = -155$ kcal./mole, which is in disagreement with the experimental value of -162.6 kcal./ mole reported by Neugebauer and Margrave. It is obvious that the results could be reconciled if either $\Delta H_{\rm f}({\rm CF_3H})$ were indeed higher as indicated above, or if $\Delta H_{\rm f}({\rm C}_2{\rm F}_6)$ were correspondingly lower (-318 kcal./ mole) then Kirkbride and Davidson reported. Thus a redetermination of these quantities may be desirable.

Table	1:	Bond Dissociation Energies and	
Heats	\mathbf{of}	Formation ^a	

$D(CF_3 - CF_3)^b$	$D(CF_{s-H})^{b}$	$\Delta H_{\rm f}({\rm CF}_{\rm d})^b$	Method	Ref.
139.5	•••	-82	Electron impact	с
122 ^d		-90.5		
124		-89.5	Electron impact	e
97'			Electron impact	g
69	102 ± 2	-117 ± 2		
65	102 ± 2	-119^{h}	H abstraction	i
77.6		-112.7		
93	109.5 ± 1.5	-105 ± 2	Bromination of CF ₃ H	j
79	102.6	-112.1	Calculated ^k	j,l
64		-119.5	Na diffusion flame	m
93 ± 4	• • •	$-105~\pm~2$	Pyrolysis	n

^a Unless otherwise stated the following heats of formation were used in these calculations: $\Delta H_f(C_2F_6) = -303$ kcal./mole and $\Delta H_f(CF_3H) = -162.6$ kcal./mole. ^b Values are in kcal./mole. ^c Ref. 1. ^d Based on $I(CF_3) = 10.10$ e.v. from ref. 5. ^e Ref. 4. ^h Based ^{*f*} Based on $A(CF_{3}^{+}) = 14.3$ e.v. from ref. 4. ^{*g*} Ref. 5. on $\Delta H_{\rm f}({\rm CF_3H}) = -169$ kcal./mole. ⁱ Ref. 7. ^j Ref. 9. * Calculated from $D(CF_3-Br) = 64.5^3$ and $\Delta H_f(CF_3Br) = -149.8$ kcal./mole.⁹ ¹ Ref. 3b. ^m Ref. 11. ⁿ This work.

In conclusion it may be stated that the result of Bibby and Carter for the C–C bond energy in C_2F_6 is much too high, which is also true of most of the other appearance potential studies and is probably due to excess kinetic or excitation energy of the ion. However, the value of Farmer, et al., although still high, is in fair agreement with our result.

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Radiation Yields of Carbon Monoxide and Dioxide for Some Aromatic Carbonyl Compounds

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An aromatic group in an organic molecule can produce opposing effects on its radiation chemistry: (a) increased stability, and (b) activation of specific bonds. These effects are illustrated in this paper by measurements of carbon monoxide and dioxide yields and ratios in the radiolysis of selected carbonyl compounds.

Experimental

Unless specified otherwise, Eastman White Label materials were used. Samples were outgassed and irradiated in a gas-measurement cell¹ with 1.5-Mev. electrons from a G.E. resonant transformer unit at an intensity of 20 Mr./min. and near room temperature. The evolved gas was analyzed in a mass spectrometer for H₂, CO, CO₂, and CH₄. The dosimetry was by an air-ionization chamber¹ and the radiation yields, G(molecules)/100 e.v., are based on an energy absorption of 1 Mr. = $6 \times 10^{19} \,\mathrm{e.v./g.}$

Results and Discussion

In Table I, the first eight esters are grouped as follows: methyl, phenyl, and benzyl acetates (1-3), benzoates (4-6), and phenylacetates (7, 8). The total gas yield, G(gas), was predominantly CO and CO₂, except for the acetates, where appreciable yields of H_2 and CH_4 were also produced. $G'(CO + CO_2)$ represents the combined yields of carbon monoxide and dioxide,

divided by the weight fraction of carboxyl, -OC=O, in the original molecule. Thus, G' measures the sensi-

⁽¹⁾ A. A. Miller, J. Am. Chem. Soc., 82, 3519 (1960).

le I :	Gas Yields for Carbonyl Compounds						
No.	Compd.	G(gas)	со	CO_2	$G'(\mathrm{CO}+\mathrm{CO}_2)$	$\rm CO/CO_2$	
1	O CH3OCCH3ª O	3.4	1.2	0.40	2.7	3.0	
2	PhOCCH ₃	2.4	1.86	0.15	6.2	13.0	
3	PhCH ₂ OCCH ₃ ^a	2.7	0.15	1.6	5.9	0.09	
4	СН3ОСРЬ	0.48	0.23	0.14	1.1	1.65	
5	PhOCPh	0.30	0.27	0.026	1.3	10.4	
6	РЬСН2ОСРЬ	0.74	0.068	0.62	3.3	0.11	
7	PhOCCH ₂ Ph ⁰	5.4	5.2	0.13	25.6	40	
8	PhCH ₂ -p-Ph-CH ₂ OCCH ₂ Ph	3.9	0.34	3.5	27.5	0.09	
9	PhCH ₂ CH ₂ OCPh	0.39	0.12	0.18	1.6	0.7	
10	$\beta - C_{10}H_7 - OCPh$	0.057	0.027	0.01	0.21	2.7	
11	PhOCOPh	2.0	1.53	0.48	7.2	3.2	
12	PhCPh	0.02	0.008	(<0.003)	0.053		
Data	from E. M. Kinderman, WADC, TR	57-465 (1957). ^b 1	These esters were	e synthesized by J	. R. Ladd and M.	J. Smith.	

Table I: Gas Yields for Ca	rbonyl Compounds
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tivity of the molecule toward radiation-induced decarboxylation, and the CO/CO_2 ratio indicates the mode of radiolysis of the carboxyl group.

In both the acetate and the benzoate series, the phenyl and the benzyl esters give higher G' values than the methyl esters. This effect can be attributed to the labilization of the adjacent bond by the phenoxy (C_6H_5O-) and the benzyl $(C_6H_5CH_2-)$ structures. Scission of the phenoxy group as a unit is evidenced by the high CO/CO_2 ratio in all of the phenyl esters.

When the carbonyl group is adjacent to and conjugated with the aromatic ring, the stability against decarboxylation is increased, as shown by a comparison of the G' values for the benzoates (4-6) with the corresponding acetates (1-3). On the other hand, when both groups adjacent to the carbonyl are phenoxy and/or benzyl (7 and 8), extremely high values of G' result. It may be noted that 2 is isomeric with 4, and 6 is isomeric with 7. In each pair, the positions of the aliphatic and aromatic groups with respect to the carbonyl are merely interchanged.

In β -phenylethyl benzoate (9), the benzyl group is separated from the carboxyl by an additional methylene unit, producing an increased stability compared with benzyl benzoate (6). For the benzoates, the change from phenyl (5) to β -naphthyl (10) increases the stability about seven fold. The lower CO/CO_2 ratio for the latter suggests also an increase in the amount of aryl, as opposed to aryloxy, scission.

In the change from phenyl benzoate (5) to diphenyl carbonate (11), the carbonyl group is no longer conjugated with either aromatic ring, resulting in a fivefold increase in G'. Conversely, conjugation of the carbonyl group with both aromatic rings greatly stabilizes the benzophenone molecule (12) against the loss of carbon monoxide.

Acknowledgments. J. R. Ladd and M. J. Smith prepared the two phenylacetate esters. Mass spectral gas analyses were done by P. C. Noble.

Molar Extinction Coefficients of O₄F₂ in the Visible Range and a Comparison with Other Oxygen Fluorides¹

by A. G. Streng and L. V. Streng

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Tetraoxygen difluoride, O_4F_2 , has been synthesized recently^{2.3} and its properties are being studied at the present time. In these studies, the molar extinction coefficients of liquid O_4F_2 have been determined. The data obtained are presented herewith.

Four oxygen fluorides, OF_2 , O_2F_2 , O_3F_2 , and O_4F_2 , are known to date. The molar extinction coefficients of O_2F_2 and O_3F_2 have been reported earlier.⁴ A literature search showed that there are no quantitative data available on the visible absorption spectrum of liquid OF_2 , in spite of the fact that this oxygen fluoride has been known since 1927.⁵ The only known data for OF_2 are the qualitative data for gaseous OF_2 .⁶ Therefore, the molar extinction coefficients of liquid OF_2 have been measured by us and are being reported here.

Experimental

Oxygen Fluorides Used. The O_4F_2 used in this study was prepared in our laboratories directly from the elements by the method described elsewhere.³ The OF_2 was a commercial product obtained from the Baton Rouge Development Laboratory, General Chemical Division, Allied Chemical Corp. It originally contained 97.7% by weight OF_2 , 1.75% O_2 , and 0.55% CO_2 and was purified by fractional distillation.

Pure undiluted liquid OF₂ and a 0.05 ± 0.01 mole/l: solution of O₄F₂ in liquid CF₄ + 3% O₂ (by volume; liquid) have been investigated at 77°K. Liquid oxygen was added to carbon tetrafluoride to avoid the solidification of CF₄ (m.p. of CF₄ is 89.2°K.).

Solvent. Carbon tetrafluoride (Freon 14) used as the solvent was a commercial product manufactured by E. I. du Pont de Nemours and Co., Inc., Wilmington, Del. It originally contained 99.74 mole % CF₄,



Figure 1. Visible absorption spectra of oxygen fluorides.

0.02% CClF₃, 0.24% air, traces of CO₂, and 10 p.p.m. of H₂O. Before use it was treated with fluorine gas at room temperature and purified by fractional distillation.

⁽¹⁾ This paper describes a part of work performed for the Office of Naval Research, Contract Nonr 3085(01).

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