Carbene-to-Carbene Oxygen Atom Transfer

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We present here evidence for carbene-to-carbene oxygen atom transfer, $R_2C: + O{=}CR'_2 \rightarrow R_2C{=}O + :CR'_2$. Singlet atomic carbon abstracts oxygen atoms from a variety of carbonyl compounds to make carbon monoxide and carbenes;[1] these highly exothermic processes can produce "hot" carbenes with unusual behavior.[2] We now report that the reactive carbenes fluorenylidene (Fl:) and methylene ($:CH_2$) behave analogously if the carbene product is sufficiently stabilized with electron donor groups (see Table 1).[3] Besides its intrinsic interest as an abstraction of a *doubly bonded* atom,[4] this reaction represents a photochemical route to nucleophilic carbenes.

Carbenes do abstract oxygen atoms from suitable donors such as *N*-oxides,[5] nitroxides,[6] carbon dioxide,[7] PF_3O,[8] or epoxides.[9] Many carbenes react with molecular oxygen to give carbonyl oxides or their isomeric dioxiranes.[10] With simple carbonyl compounds such as aldehydes,[11] ketones,[12] esters,[13] amides,[14] and ureas,[15] electrophilic singlet carbenes attack the oxygen lone electron pairs to form carbonyl ylides **1**. These intermediates may then cyclize to form epoxides[16] or undergo cycloaddition with a second equivalent of carbonyl compound to give dioxolanes.[11,12g] A third, almost unexplored, pathway is fragmentation to a new carbene/carbonyl compound pair. Indeed, Warkentin *et al*. have shown[17] that explicit synthesis

Table 1. Thermochemistry of Oxygen Donors and Selected Rate Constants for Their Reactions with Fluorenylidene

	ΔH^a					k_{XO}(LFP)
X:	X:	XO	BDE[b]	CSE[c]	k_{XO}/k_{MeOH}	$\times 10^{-8\ d}$
^{1}:C:	201	−26	286	51		
^1H_2C:	102	−26	187	0		
Fl:	133[e]	13[f]	179	9		
F_2C:	−45	−153	168	57		
$(MeO)_2C$:	−35[g]	−139	163	92	$(1.2\pm0.2)\times10^{-3}$	0.01
$(H_2N)_2C$:	39[h]	−59	158	79		
$(Me_2N)_2C$:	44[i]	−57	160	72	$(4.9\pm0.2)\times10^{-1}$	2.6 (3)
$C_2H_4(NMe)_2C$:	56[i]	−41	156		$(5.2\pm0.2)\times10^{-1}$	2.8
:CO	−26	−94	127	120		
$(MeO)_3P$:	−167	−265	158		$(1.4\pm0.2)\times10^{-2}$	0.8
C_4H_8SO	−35	−88	113			
Z-2-butene	−2	−30	88			3
E-2-butene	−3	−31	88			9
C_5H_5N:	33	14	79		1.7 ± 0.4	9 (4.8)
4-MeC_5H_4N:	25	6	79		1.7 ± 0.4	9

[a] Unless otherwise noted, these are ΔH_f values at 298 K, from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas Phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data* **1988**, *17* (Suppl. 1). [b] BDE = bond dissociation energy; note that ΔH_f for oxygen is 59.6 kcal/mol at 298 K. [c] CSE = carbene stabilization energy, defined as $\Delta H(:CH_2 + CX_2H_2 \rightarrow CH_4 + :CX_2)$. [d] Referenced to $k_{MeOH} = 5 \times 10^8$ M^{-1} s^{-1}, obtained with the same LFP and protocol (ylide probe method) as the O-donor rate constants; this value is less than literature values ($\sim 9 \times 10^8$ M^{-1} s^{-1}; see ref 19). [e] From MP2/6-31G*//HF/6-31G* energies for X-transfer from FlX to $:CH_2$, with experimental ΔH_f values for the reference compounds, we estimate ΔH_f(Fl:) = 129 and 136 kcal/mol for X = O and X = H_2, respectively; the listed value is an average. A previously cited value of 156 kcal/mol (Li, Y.; Schuster, G. B. *J. Org. Chem.* **1988**, *53*, 1273) was estimated from the semiempirical AM1 calculations. [f] Sabbah, R.; Watik, L. E.; Minadakis, C. *C. R. Acad. Sci., Ser. II* **1988**, *307*, 239. [g] From calculated proton affinity (234 kcal/mol at MP3/6-31+G*//HF/6-31+G*+scaled ZPE) and the experimental ΔH_f (97 kcal/mol) of $(MeO)_2CH^+$. The MP2/6-31G*//HF/6-31G*+scaled ZPE reaction energies for $F_2C: + (MeO)_2C{=}O \rightarrow F_2C{=}O + (MeO)_2C:$ and $(H_2N)_2C: + (MeO)_2C{=}O \rightarrow (H_2N)_2C{=}O + (MeO)_2C:$ give similar results, −31 and −35 kcal/mol, respectively. The agreement among these three independent calculations brings into question the −61 kcal/mol reported in an earlier experimental study (see ref 22). [h] McGibbon, G. A.; Kingsmill, C. A.; Terlouw, J. K. *Chem. Phys. Lett.* **1994**, *22*, 129−34. [i] Substituted diaminocarbene ΔH_f values were estimated via experimental values and the MP2/6-31G*//HF/6-31G*+scaled ZPE reaction energies for oxygen exchange with urea.

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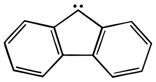
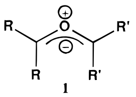
of ylide **1** ($R = CH_3$, $R' = OCH_3$), via oxadiazoline decomposition, leads to acetone and dimethoxycarbene products.



Fl:

:CH$_2$



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In this work, fluorenylidene (Fl:) and methylene (:CH$_2$) have been examined as oxygen abstractors. The carbenes were photolytically generated from diazofluorene (DAF) and diazomethane, respectively, and their reactions were studied by product analysis and laser flash photolysis (LFP). LFP studies of Fl: via the ylide probe method[18] work well, and the oxygenation product fluorenone (Fl═O) is easily detected. Despite its triplet ground state, Fl: generally shows singlet behavior because of the high reactivity of its singlet state and its small singlet−triplet gap (1.1 kcal/mol).[19] Similarly, singlet reactivity dominates the chemistry of :CH$_2$ in condensed phases due to the singlet's high reactivity and relatively slow rate of intersystem crossing to the triplet ground state.[20]

Product Studies. In dry degassed acetonitrile or benzene, Fl: is oxygenated by pyridine-*N*-oxide (PNO), 4-picoline-*N*-oxide, *N*-methylmorpholine-*N*-oxide and *cis*- and *trans*-2-butene oxides[9] to give Fl═O; minor byproducts are bifluorenyl, bifluorenylidene, and, in some cases, products of reaction with solvent.[21] The poorer oxygen donors—dimethyl carbonate, sulfolane, and trimethyl phosphate—gave similar results when used neat. Yields of Fl═O were substantial, ranging from 30% to 90% based on DAF.

Considering the stability (see Table 1) of diamino-[3] and dialkoxycarbenes,[22] we examined tetramethylurea (TMU), 1,3-dimethylimidazolidin-2-one (DMI), and dimethyl carbonate (DMC) as substrates.[23] Like the more traditional oxidants, they reacted with Fl: to give Fl═O. The use of ^{18}O-labeled TMU,[24] with product analysis by GC−MS,[25] confirmed that the oxygen in the product Fl═O came from the carbonyl substrate.

The above results implicate the corresponding stabilized carbenes as byproducts in the urea and carbonate deoxygenations. In the TMU deoxygenation, our attempts to trap the bis(dimethylamino)carbene with alkenes such as cyclohexene, dimethyl fumarate, acrylonitrile, or norbornadiene were unsuccessful; only Fl: addition products were detected. Such highly stabilized carbenes do not react significantly with simple olefins, preferring to dimerize instead. The more electron-deficient alkenes, appropriate for trapping nucleophilic carbenes, also undergo 1,3 dipolar cycloaddition with DAF, destroying the carbene precursor and leading ultimately to fluorene-containing cyclopropane products. Trapping with alcohols or water yielded more promising results; GC−MS peaks corresponding to the O−H insertion products were observed, but these hydrolytically sensitive materials were not isolated.

Like dimethoxycarbenes,[17] in the absence of traps, the bis(dimethylamino)carbenes generated by TMU deoxygenation dimerize.[3] The resulting tetrakis(dimethylamino)ethylene reacts rapidly when exposed to O$_2$ at room temperature to produce TMU (as in our ^{18}O-TMU synthesis)[24] and *visible light*. This characteristic chemiluminescence verified the presence of carbene dimer when air was bubbled through photolyzed samples of DAF in neat TMU inside a fluorimeter cavity.[26] Neither photolyzed samples of TMU without DAF nor unphotolyzed DAF-containing samples showed chemiluminescence. The same kind of analysis demonstrated that :CH$_2$, generated by photolysis of diazomethane, also abstracts oxygen from TMU.

Rate Studies. Absolute rate constants for Fl: reaction with oxygen donors were measured by LFP using the ylide probe method[18] (see Table 1). Competition with insertion into methanol O−H bonds allowed additional rate constants to be calculated via the absolute rate constant for Fl: quenching with methanol in acetonitrile.[27] Table 1 shows that LFP and competition-derived rate constants compare reasonably well; as expected, the reactivities of oxygen donors with Fl: track inversely with C═O bond strengths.

In summary, carbene-to-carbene oxygen atom transfer has been demonstrated by isotopic labeling and by observation of products from the newly generated carbene. Rate constants for oxygen abstraction by Fl: from various donors, including ureas, have been determined. Whether these highly exothermic oxygen transfers occur in a single step or via the intermediacy of ylide or oxirane intermediates is a question that is under active study. A later report will describe detailed ab initio molecular orbital studies of the remarkably convoluted potential energy surfaces for carbene-to-carbene oxygen transfer reactions.

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(21) Given the checkered history of the ylide formed from Fl: and acetonitrile (see: Platz, M. S. Reference 4d, pp 285−287 and references therein), we explicitly generated this species by photolysis of the corresponding azirine precursor in the presence of PNO to verify that PNO oxygenation of this ylide could not make the Fl═O observed. In any case, subsequent rate studies showed that, in the concentration ranges studied, the acetonitrile ylide formation could not compete.

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(23) Attempts to form and detect stable carbenes from 1,3-di-*tert*-butylimidazolidin-2-one or tetraisopropylurea are underway. We thank Professor R. W. Alder for sharing results (*Angew. Chem*., in press) on these new systems prior to publication.

(24) ^{18}O-TMU was obtained in near quantitative yield by reaction of $^{18}O_2$ with the electron-rich olefin tetrakis(dimethylamino)ethylene (TDA). Alkene was added to a flask charged with $^{18}O_2$, stirred 1−2 h, distilled, and chromatographed. The final ^{18}O content was 95% by GC−MS.

(25) The expected product of ^{18}O transfer, labeled Fl═^{18}O, was detected via GC−MS of the reaction mixture. In the experiments to date, the fluorenone was found as a mixture of Fl═^{18}O and Fl═^{16}O in a 1:3 ratio. We believe that Fl═^{16}O results from reaction of traces of $^{16}O_2$ with Fl: either in the reaction mixture or (from residual DAF) in the injector of the GC−MS. Refinement of this protocol, specifically by improvement of our vacuum system for freeze−pump−thaw degassing, is underway.

(26) Emission spectra were identical for our samples and authentic TDA in the same solvents. The emission is structureless, with a broad maximum centered at 515 nm. See: Winberg, H. E.; Downing, R. E.; Coffman, D. D. *J. Am. Chem.. Soc.* **1965**, *87*, 2054−55.

(27) Ratios of Fl═O to 9-methoxyfluorene product were determined by NMR and/or GC analyses. Several ratios of oxygen donor to methanol were examined to ensure that observed product ratios reflected direct reactions of Fl: with substrates and not indirect pathways to the same products.