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Structural Influences on the Chemical Reactivity of Hydrocarbons Toward Nucleogenic Carbon Atoms

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ABSTRACT

A systematic measurement of the kinetic rate constant ratios for nucleogenic ground-state carbon-11 atom reactions with either a hydrocarbon or molecular oxygen has provided a means to intercompare the relative reactivities of several saturated, unsaturated and aromatic hydrocarbons and provide insight relating molecular structure with chemical reactivity at high kinetic energies. We noted from these studies that saturated aliphatic hydrocarbon reactivities tended to increase with size of the carbon skeleton relative to methane. We also noted that unsaturated aliphatic hydrocarbons were significantly more reactive than their saturated counterparts owing to the propensity for ground-state carbon atoms to react at the π-bond. This action was exemplified by a 14.5-fold increase in ethylene reactivity over ethane. However, alkyl substituents lowered the magnitude of this effect. This behavior may be due in part to bond stabilization through electron delocalization, and in part to steric effects. This later effect was evident by the fact that *cis*-2-butene was twice as reactive as its *trans*-isomer. Interestingly, resonance stabilization carried to the extreme of aromatic behavior will render the molecule no more reactive than a saturated hydrocarbon of equivalent size. We noted that electron donating groups decreased reactivity while electron withdrawing groups especially in the meta position on the ring increased reactivity. This behavior seems atypical of what one would expect of an electrophilic reagent.

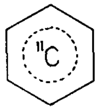
INTRODUCTION

Gas-phase studies delineating the kinetics and mechanisms of recoil carbon-11 atom reactions in aromatic systems provide a basis to extend the understanding of carbon atom chemistry beyond the scope of simple aliphatic systems investigated over the last three decades. These earlier studies utilized a variety of experimental methods that included nuclear recoil,[1-4] thermal evaporation,[5] thermal decomposition,[6] and photochemical decomposition.[7,8] As a result of these studies, the quadravalent carbon atom was predicted to undergo a set of characteristic reactions in order to reduce its electron deficiency. These reactions included: (i) insertion into C-H bonds, [9-11] (ii) addition to carbon-carbon double bonds,[12-14] and (iii) abstraction of hydrogen from hydrocarbons.[15-20] Nuclear recoil studies have provided considerable insight into a number of features of these reactions,[21,22] some of which included the nature of reaction intermediates,[23-25] and the effects of translational energy[26-30] and carbon atom electron spin state [25,28,29] on chemical reactivity and product stability. Photochemical studies have also provided absolute rate constants for a number of these reactions where ground state $C(^3P)$ and first excited state $C(^1D)$ atoms were monitored in the presence of various hydrocarbons.[30-33]

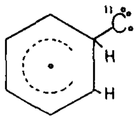
Unlike the simpler aliphatic systems, past investigations on carbon atom-aromatic hydrocarbon reactions have not provided us with as in depth an understanding of the chemistry. These studies have mostly been restricted to recoil carbon atom reactions in the condensed phase and, furthermore, to the elucidation of complex product spectra.[34-40] Some investigations have attempted to delineate principal features, such as translational energy and electronic spin states affecting carbon atom reactivity with simple aromatic hydrocarbons.[36,41] Major questions were raised, however, concerning which bonds on an aromatic molecule present active sites for carbon atom attack. Even after thirty years, these questions still remain unanswered.

The π-electrons and C-H bonds of an aromatic molecule should both offer attractive sites for attack by an electron deficient carbon atom. Previous studies on the chemistry of recoil carbon-11 atoms with ethylene have demonstrated that the reaction can proceed at either the C-H or π-bonds to yield 1-[^{11}C]-allene and 2-[^{11}C]-allene, respectively, as dominant products.[13,28] However, the availability of each site to attack was found to be extremely sensitive to the translational energy of the carbon atom and to its electronic spin state.[28] Additional studies on the reactions of carbon-11 atoms with 1,3-butadiene[42] and cyclohexadiene[43] have also shown chemistry characteristic of the same fundamental processes observed in the simple ethylene system.

Mechanistic considerations become somewhat more complex when addressing carbon atom reactions with aromatic molecules. A number of stable adducts have been proposed to account for the extensive rearrangements in the reactions of carbon-11 atoms with benzene.[41,44] These adducts included the following: a random π-bond complex (I); a sigma-complex (II) arising from π-addition; norcaradienylidene (III) arising from 1,2-addition across the π-bond; and phenylmethylene (IV) arising from insertion into a C-H bond. Results obtained in carbon-14 chemical accelerator studies also suggested a 1,3-bicyclic C_7 intermediate to account for the [^{14}C]-labelling distribution in some primary products.[45]



I



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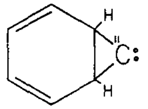
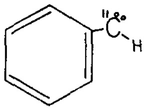


III



IV

Additional studies utilizing double tracer techniques focussed on the reactions of carbon-11 atoms with various deuterated benzenes, and on the extent of deuterium incorporation in [^{11}C]-acetylene arising from decomposition of the C_7 adduct.[46] Results from these studies ruled out the possibility of random π-complex (I) formation and suggested that the C_7 adduct is formed as a result of direct attack at one of the chemical bonds.

In 1986, an investigation was initiated to determine whether tolylmethylenes were generated as intermediates subsequent to the gas-phase attack by recoil carbon-11 atoms with toluene.[47] The methyl group of this molecule acted as a trap to convert the reactive [^{11}C]-moieties into [^{11}C]-styrene and [^{11}C]-benzocyclobutene. Degradation of each product revealed the distribution of the carbon-11 label which allowed a number of conclusions to be drawn. [^{11}C]-Styrene was predominantly formed in the rearrangement of benzylmethylene arising from insertion into the C-H bond of the methyl group in toluene. On the other hand, ring attack yielded tolylmethylenes which rearranged almost exclusively to [^{11}C]-benzocyclobutene. The experimentally measured distribution of [^{11}C]-label in this product coincided well with the statistical distribution of label expected from exclusive ring C-H insertions. These results strongly suggested, at least in the formation of styrene and benzocyclobutene, that the π-electrons of toluene were not primary sites for carbon atom attack.

The present investigation reports results from a systematic kinetic investigation, measuring carbon atom reactivities toward saturated, unsaturated and aromatic hydrocarbons, that provides new insight into structural effects on π-bond reactivity. Competition experiments in binary hydrocarbon-oxygen mixtures buffered in xenon gas were carried out in order to measure and compare the relative reactivities of non-thermal ground-state carbon-11 atoms. In studying the competition reactions of these species, oxygen was selected as a suitable competing second substrate because its reaction yields [^{11}C]-carbon monoxide as the only non-thermal product,[4,23,48,49] and because this product is readily distinguished from the [^{11}C]-products arising from carbon atom reactions with the hydrocarbon substrate. In all systems studied, hot [^{11}C]-carbon monoxide yields were measured as a function of oxygen concentration in the hydrocarbon/oxygen gas mixtures. These data were then applied to the Estrup-Wolfgang kinetic theory of hot-atom reactions to arrive at the ratios of the cross section weighted reactivity integrals between oxygen and appropriate hydrocarbon.[50,51] However, by virtue of their nucleogenesis, carbon-11 atoms can be expected to occupy a mixed population of low lying electronic spin states; ^{3}P(O eV), ^{1}D(1.7 eV) and ^{1}S(2.3 eV). This unknown variable can overshadow any kinetic interpretations of the data. However, gross changes in the distribution of electronic states can be imposed through the addition of xenon to recoil reaction mixtures.[26-29,42,52] Efficient quenching of electronically excited carbon atoms can be effected through collisions with xenon yielding a population of atoms that reside predominantly in their ground-state. Thus, by blanketing the hydrocarbon-oxygen systems in a xenon buffer, a high population of the ^{3}P ground-state carbon atom can be produced and the kinetic interpretation of the data simplified. Granted, this methodology may not be considered ideal from the stand-point of a true kineticist. Then again, our intent here is not to measure precise rate constants, but rather to observe, and correlate differences in hydrocarbon reactivity integrals with hydrocarbon structure. It is also worth noting that the nuclear recoil technique is unique in its ability to impart excess kinetic energy to the atomic species, and thus affords a unique look at chemical reaction mechanisms as well as chemical reactivity at kinetic energies unmatched by any other technique.

EXPERIMENTAL

Materials. Hydrocarbon gases used in the target system were purchased from Matheson Gas Co. and included methane (min. 99.99% purity), ethane (min. 99.99% purity), propane (99.97%), n-butane (99.9% purity), ethylene (min. 99.99% purity), allene (93% purity) and 1,3-butadiene (99.8% purity). Benzene and toluene were purchased from Mallinckrodt. All hydrocarbons were degassed prior to use by conventional vacuum line techniques. Research grades for oxygen (Matheson > 99.98% purity) and xenon (Matheson 99.999%) were used in all cases without further purification to make up the gas mixtures.

Sample Preparation. Samples were prepared for irradiation by first filling a desired pressure of hydrocarbon into an evacuated 30 mL quartz irradiation vessel equipped with a Teflon-brand stopcock. Higher pressures of oxygen were then added to attain the desired composition of gases. In all instances, the total pressure of the hydrocarbon-oxygen mixture was maintained at 40 Torr. Finally, higher pressures of xenon gas were added in order to bring the target total pressure up to 1 atmosphere thus yielding a xenon buffer of approximately 95% of the gas composition.

Irradiations. The irradiations were carried out using a 33 MeV proton beam from the Brookhaven 60-inch cyclotron. Recoil carbon-11 atoms were generated predominantly by the ^{12}C(p,pn)^{11}C nuclear transformation, but some contribution from the ^{16}O(p,pαn)^{11}C transformation was noted in these binary gas samples. The proton beam penetrated the static quartz targets through an 0.01-inch quartz window without significant degradation in energy. Typical beam intensities were 1 μA with exposure times of 60 s. Radiation doses were generally between 0.3×10^{-3} and 1.1×10^{-3} eV molecule-1 μA^{-1} s^{-1}, as determined by acetylene to benzene dosimetry.[53]

Radioassay of ^{11}C Activity. Following the irradiation, a 1 mL aliquot of the target gas was withdrawn through a septum on the vessel using Teflon-brand sealed gas syringe (Precision Sampling Corp.) The aliquot was injected into a radio gas chromatograph for analysis of the [^{11}C]-carbon monoxide yield. A 12-ft glass column packed with 80-100 mesh Porapak N (Analabs Inc.) provided excellent separation of the carbon monoxide peak from the remaining hydrocarbon product spectrum. The radioactive compounds eluting from the column were measured using a gas effluent proportional counter[54] interfaced with an IBM PC computer through Canberra counting electronics. This provided on-line acquisition and reduction of data.

A second 1 mL aliquot of the target gas was withdrawn in the same manner, however, this aliquot was injected into a preevacuated 10 mL tube equipped with a septum, and counted using a well-type NaI (Tl) scintillation crystal to provide a measure of the total volatile carbon-11 activity (TVA). The nonvolatile products deposited on the inside walls of the target were also extracted through sequential washings with acetone and hexane. The combined washings were counted to provide a measure of the nonvolatile activity (NVA). The total carbon-11 activity (TA) was determined by summing the TVA and VA measurements after appropriate radioactive decay and fraction corrections were made. The [^{11}C]-carbon monoxide yield was calculated as an absolute yield by dividing the decay-corrected integrated peak activity from the effluent counter by the TA.

RESULTS AND DISCUSSION

In Tables 1-3, the yield of ^{11}CO is presented as a function of the binary gas composition of hydrocarbon-oxygen for saturated, unsaturated and aromatic molecules. Previous studies performed at this laboratory in alkane-oxygen systems have reported similar ^{11}CO yields, however, the present studies represent a complete investigation in the high oxygen concentration range necessary to apply an appropriate hot atom kinetic treatment.[48,49]

It is implicit in the mechanistic hypothesis that provides a basis for our kinetic treatment of the data, that ^{11}CO is exclusively formed through the reaction of carbon-11 atoms with oxygen. A trace amount of $^{11}CO_2$ was observed in all systems studied, but its yield was insensitive to changes in the oxygen concentration. Possible sources for this product include radiolytic oxidation of ^{11}CO,[55] or perhaps wall release of $^{11}CO_2$ from beam penetration of the target quartz window.[56] Of the two, the later source seems more consistent with the product's insensitivity to oxygen concentration, and allows us to ignore $^{11}CO_2$ in the treatment. An assumption is also made that transient species such as ^{11}CH and $^{11}CH_2$ do not react with oxygen to yield ^{11}CO.[57]

The treatment of systems containing a mixture of two components both of which can react with the hot atom is complex. In the present treatment we must consider a system comprised of two reactive components, namely O_2 and RH. The yield of hot products arising from reaction with O_2 is fortunately limited to only ^{11}CO. Thus we can write the basic equation for the probability (i.e. fractional yield) of reaction with the hydrocarbon reactant, RH as:

$$P_{RH} = \int_{E_1}^{E_2} \frac{f_{RH}\ \rho_{RH}}{\alpha E} \exp\left(-\int_{E}^{E_2} \frac{f_{RH}\rho_{RH} + f_{O_2}\rho_{O_2}}{\alpha E}\, dE\right) dE \qquad (1)$$

Table 1

Yields of ^{11}CO from Alkane-Oxygen Mixtures[a,b]

Methane			Ethane			Propane			n-Butane			Pentane		
[RH]	[O$_2$]	Yield ^{11}CO	[RH]	[O$_2$]	Yield ^{11}CO	[RH]	[O$_2$]	Yield ^{11}CO	[RH]	[O$_2$]	Yield ^{11}CO	[RH]	[O$_2$]	Yield ^{11}CO
99.4	0.6	56.6±1.6	99.4	0.6	53.5±0.8	97.3	2.7	42.7±0.3	96.7	3.3	40.0±0.4	93.7	6.3	38.7±1.2
98.8	1.2	60.0±1.9	98.8	1.2	62.9±5.0	94.6	5.4	51.4±0.5	93.3	6.7	51.5±0.5	88.3	11.7	40.6±0.6
98.2	1.8	65.6±2.1	98.3	1.7	65.7±2.4	92.3	7.7	54.2±0.3	89.7	10.3	53.0±0.6	73.7	26.3	52.4±0.7
96.1	3.9	70.5±1.1	97.8	2.2	63.5±1.2	90.9	9.1	55.6±0.6	86.7	13.3	56.0±0.4	67.1	32.9	58.7±0.9
95.1	4.9	77.0±0.9	94.0	6.0	69.9±2.0	90.2	9.8	56.2±0.3	86.0	14.0	57.8±0.4	60.9	39.1	60.0±0.3
93.4	6.6	79.0±1.5	93.7	6.3	70.9±4.0	87.4	12.6	61.2±0.2	80.7	19.3	61.8±0.4	54.7	45.3	64.9±0.5
92.5	7.5	80.8±3.2	91.9	8.1	77.2±1.6	83.5	16.5	63.4±0.4	73.5	26.5	67.7±0.8	48.6	57.4	72.2±0.5
84.0	16.0	88.7±1.4	90.0	10.0	80.3±1.9	77.0	23.0	69.1±0.5	63.9	36.1	73.8±0.1	41.6	58.4	76.6±0.6
71.6	28.4	92.4±1.5	85.2	14.8	81.9±0.6	73.6	26.4	75.5±0.5	56.4	43.6	78.8±1.2	31.5	68.5	83.1±1.8
58.7	41.3	93.4±1.0	80.5	19.5	85.2±3.7	66.2	33.8	81.6±0.6	46.3	53.7	82.5±1.8			
50.9	49.1	95.5±1.2	72.8	27.2	87.2±5.0	48.7	51.3	91.4±0.6	29.3	70.7	92.6±1.9			
46.0	54.0	95.1±1.2	69.6	30.4	84.5±1.8	40.4	59.6	93.2±0.7						
40.0	60.0	95.9±2.9	60.8	39.2	86.7±4.9	32.6	67.4	95.8±1.0						
27.1	72.9	98.2±1.8	40.1	59.9	92.7±2.8	25.3	74.7	96.0±1.3						
			32.4	67.6	96.1±3.9									
			21.8	78.2	97.6±3.3									

a. [RH] and [O$_2$] values are percent concentrations relative to 40 Torr partial pressure.

b. Yields of ^{11}CO are absolute based on total ^{11}C-activity produced.

Table 2

Yields of ^{11}CO from Alkene-Oxygen Mixtures[a,b]

Ethylene			Allene			1,3-Butadiene			*cis*-2-Butene			*trans*-2-Butene		
[RH]	[O$_2$]	Yield ^{11}CO	[RH]	[O$_2$]	Yield ^{11}CO	[RH]	[O$_2$]	Yield ^{11}CO	[RH]	[O$_2$]	Yield ^{11}CO	[RH]	[O$_2$]	Yield ^{11}CO
93.3	6.7	17.9±0.3	93.6	6.4	16.9±0.4	75.7	24.3	32.3±0.4	93.3	6.6	21.7±0.3	93.4	6.6	29.7±0.3
86.7	13.3	26.8±0.3	86.6	13.4	37.2±0.5	68.1	31.9	36.9±0.4	86.8	13.2	27.2±0.3	86.7	13.3	32.1±0.3
80.4	19.6	29.8±0.4	79.6	20.4	44.8±0.6	61.2	38.8	45.1±0.7	80.4	19.6	26.6±0.3	80.3	19.7	35.5±0.3
73.3	26.7	32.6±0.4	75.8	24.2	43.6±0.4	55.6	44.4	50.3±0.4	66.8	33.2	35.1±0.3	73.5	26.5	45.7±0.4
64.4	33.6	40.6±0.4	68.2	31.8	51.8±0.1	51.1	48.9	55.7±0.5	60.8	39.2	41.8±0.3	61.6	38.4	55.3±0.4
58.2	41.8	45.8±0.6	61.9	38.1	50.3±0.6	38.5	61.2	65.5±0.6	54.0	46.0	50.7±0.5	49.5	50.5	64.8±0.6
40.6	59.4	56.4±0.6	57.1	42.9	58.5±0.8	34.5	65.5	73.6±0.6	48.1	51.9	55.3±0.5	40.0	60.0	73.4±0.6
32.0	68.0	64.6±0.9	55.1	44.9	60.3±0.5	27.2	72.8	77.3±0.9	40.3	59.7	62.7±0.6	33.8	66.2	79.5±0.7
29.7	70.3	66.4±1.2	47.4	52.6	67.8±0.6	25.7	74.3	77.5±0.8	30.7	69.3	65.5±0.6	22.4	77.6	86.4±0.9
22.1	77.9	73.7±1.2	40.8	59.2	73.4±0.6				20.4	79.6	78.8±0.8			
			34.2	65.8	77.9±0.7									
			31.6	68.4	80.6±0.9									
			24.1	75.9	85.9±1.1									

a. [RH] and [O$_2$] values are percent concentrations relative to 40 Torr partial pressure.

b. Yields of ^{11}CO are absolute based on total ^{11}C-activity produced.

Table 3

Yields of ^{11}CO from Aromatic Hydrocarbon-Oxygen Mixtures[a,b]

Benzene			Toluene			Trifluorotoluene			Fluorobenzene			o-Difluorobenzene			m-Difluorobenzene		
[RH]	$[O_2]$	Yield ^{11}CO	[RH]	$[O_2]$	Yield ^{11}CO	[RH]	$[O_2]$	Yield ^{11}CO	[RH]	$[O_2]$	Yield ^{11}CO	[RH]	$[O_2]$	Yield ^{11}CO	[RH]	$[O_2]$	Yield ^{11}CO
71.2	28.8	48.9±0.5	92.3	7.7	29.7±1.1	89.5	10.5	34.8±0.9	86.7	13.3	33.7±0.7	85.0	15.0	45.1±0.8	87.3	12.7	23.2±0.6
63.3	36.7	52.2±0.5	84.6	15.4	39.4±1.0	78.9	21.1	41.8±0.9	75.4	24.6	43.7±1.0	70.0	30.0	59.3±1.5	71.4	28.6	47.1±0.6
62.0	38.0	60.7±0.5	80.4	19.6	40.4±1.0	68.5	31.5	46.3±0.8	59.0	41.0	49.3±1.0	55.0	45.0	63.9±2.0	58.7	41.3	51.9±1.0
58.5	41.5	60.8±0.5	76.9	23.1	56.5±1.3	58.6	41.4	65.4±0.8	50.8	49.2	60.6±0.8	45.0	55.0	70.3±1.8	47.7	52.3	62.2±1.7
55.8	44.2	61.7±0.5	68.6	31.4	52.7±0.9	48.3	51.7	71.0±1.2	41.0	59.0	63.7±1.0	35.0	65.0	76.9±1.5	41.5	58.5	57.7±0.9
45.5	54.5	70.6±0.8	59.1	40.9	63.9±1.1	37.9	62.1	75.9±1.0	37.7	62.3	67.3±1.0	25.0	75.0	82.7±1.9	35.4	64.6	66.5±2.0
39.6	60.4	80.4±0.5	54.6	45.4	68.4±1.3	31.0	69.0	81.7±0.8	31.2	68.8	70.6±1.3				26.2	73.8	73.3±0.9
31.3	68.7	83.8±0.5	50.0	50.0	80.2±0.8				26.2	73.8	77.0±1.3				23.1	76.9	74.7±1.3
31.1	68.9	83.6±0.7	45.5	54.5	83.0±1.4												
25.9	74.1	87.5±0.8	40.9	59.1	85.6±1.6												
			36.4	63.6	87.1±1.8												

a. [RH] and $[O_2]$ values are percent concentrations relative to 40 Torr partial pressure.

b. Yields of ^{11}CO are absolute based on total ^{11}C-activity produced.

The term f_i, the collision fraction, is defined as the relative probability of collision with reactant i, and can be written as:

$$f_i = \frac{\sigma_i \chi_i}{\sum \sigma_i \chi_i} \tag{2}$$

where σ_i is the reaction cross section for i, and χ_i is the mole fraction of i. The α term in equation 1 relates the average logarithmic energy loss per collision with i and can be written as:

$$\alpha = f_{RH}\,\alpha_{RH} + f_{O_2}\,\alpha_{O_2} \tag{3}$$

We have chosen to ignore the energy losses per collision with xenon since its composition was always a fixed parameter in these studies. Finally, the ρ_i term in equation 1 is defined as the probability of chemical combination on collision with i where

$$\rho_i(E) = \frac{\sigma_i^{react}}{\sigma_i} \tag{4}$$

is the probability of reaction with i on collision at some energy E.

Expanding the exponential in equation 1 and keeping only the leading constant term (unity) gives for the fractional yields

$$P_{RH} \approx \frac{f_{RH}}{\alpha} I_{RH} \text{ and } P_{O_2} \approx \frac{f_{O_2}}{\alpha} I_{O_2} \tag{5}$$

where I_i is the reactivity integral for i and is equal to:

$$I_{RH} = \int_{E_1}^{E_2} \frac{P_{RH}(E)}{E}\, dE \quad \text{and} \quad I_{O2} = \int_{E_1}^{E_2} \frac{P_{O2}(E)}{E}\, dE \tag{6}$$

for the two reactants. This gives:

$$\frac{1}{P_{RH}} \approx \frac{\alpha_{RH}}{I_{RH}} + \frac{\alpha_{O2}}{I_{O_2}}\,\frac{f_{O_2}}{f_{RH}} = \frac{\alpha_{RH}}{I_{RH}} + \frac{\sigma_{O_2}\alpha_{O_2}}{\sigma_{RH}I_{RH}}\left(\frac{\chi_{O_2}}{\chi_{RH}}\right) \tag{7}$$

and

$$\frac{1}{P_{O_2}} \approx \frac{\alpha_{O_2}}{I_{O_2}} + \frac{\alpha_{RH}}{I_{O_2}}\,\frac{f_{RH}}{f_{O_2}} = \frac{\alpha_{O_2}}{I_{O_2}} + \frac{\sigma_{RH}\alpha_{RH}}{\sigma_{O_2}I_{O_2}}\left(\frac{\chi_{RH}}{\chi_{O_2}}\right) \tag{8}$$

Both equations should be linear. In fact, we found equation 8 to be extremely useful as a consistency check for data selection in the kinetic analysis, where plots of $1/Y_{^{11}CO}{}^{hot}$ versus $\chi RH/\chi O2$ should be linear in the range of analysis. More importantly, the intercept $\alpha O_2/IO_2$ should be constant from system-to-sytem.

Dividing one linear equation by another can lead to the expression

$$\frac{P_{O_2}}{P_{RH}} = \frac{f_{O_2}\, I_{O_2}}{f_{RH}\, I_{RH}} \tag{9}$$

or

$$\frac{P_{O_2}}{P_{RH}} = \frac{\alpha_{O_2}\, I_{O_2}}{\alpha_{RH}\, I_{RH}}\left(\frac{\chi_{O_2}}{\chi_{RH}}\right) \tag{10}$$

Thus a plot of $Y_{^{11}CO}{}^{hot}/1\text{-}Y_{^{11}CO}{}^{hot}$ versus χ_{O_2}/χ_{RH} should yield a straight line whose slope is simply the ratio of the cross section weighted reactivity integrals for reaction with oxygen versus hydrocarbon.

The treatment of the yield data in Tables 1-3 by equation 10 can be seen in Figures 1a, 2a and 3a for the saturated, unsaturated and aromatic hydrocarbon systems, respectively. Only those data points used in the analysis were shown graphically. Linear regression analysis of these treatments yielded $\sigma_{O_2}I_{O_2}/\sigma_{RH}I_{RH}$ values which were tabulated in column 2 of Table 4. In most cases, the R squared correlation on the regression analysis was 0.98 to 0.99. However, as a selection criteria for obtaining the best fit in this analysis, the same data from Tables 1-3 was plotted according to equation 8 and depicted in Figures 1b, 2b and 3b. Interestingly, much of the ^{11}CO yield data in the low oxygen concentration range had to be discareded from all systems (and is not shown graphically), because of deviation from linearity in the selection criteria. This was very obvious in the less reactive saturated hydrocarbon systems. The reasons for such deviations is due to the fact that the less reactive hydrocarbons are behaving like energy moderators of the hot atoms, and thus the rapid rise in ^{11}CO yield at low oxygen concentration is simply due to oxygen's high eficiency to scavenge these thermalized carbon-11 atoms. Thus, we wanted to restrict our analysis only to those regions of high energy. As an example

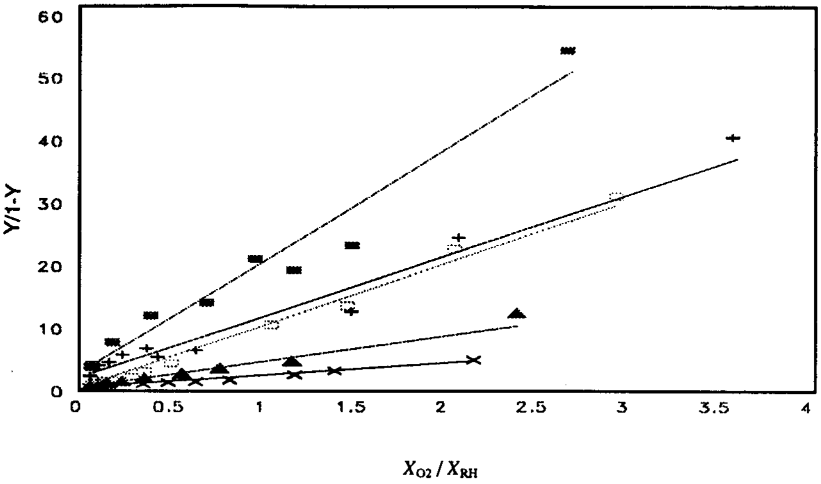


Figure 1a. Kinetic treatment of hot ^{11}CO yield data from alkane/oxygen sytems buffered in xenon moderator where the slope equals $\sigma_{O2}\, I_{O2}/\sigma_{RH}\, I_{RH}$, (methane, ■ ; ethane, + ; propane, □; butane, ▲ ; pentane, x).

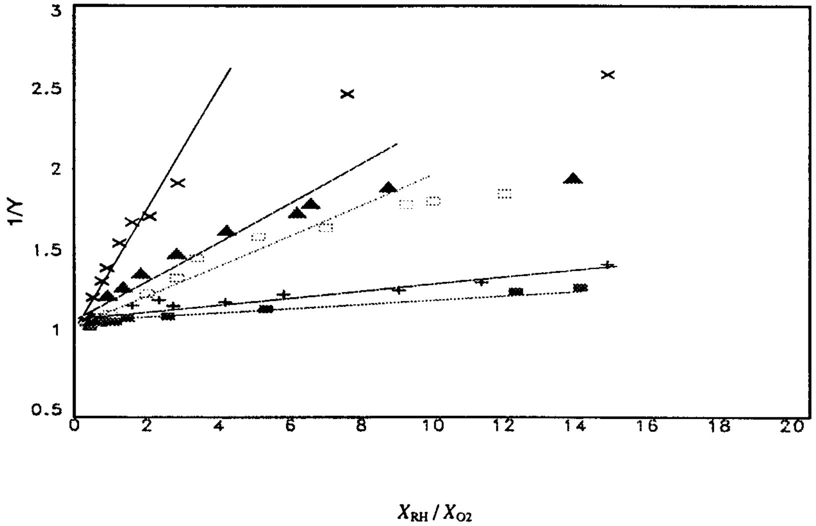


Figure 1b. Data consistency check and selection criteria for alkane/oxygen systems based on linearity and a constant intercept of α_{O2}/I_{O2}, (methane, ■; ethane, + ; propane, □ ; butane, ▲; pentane, x).

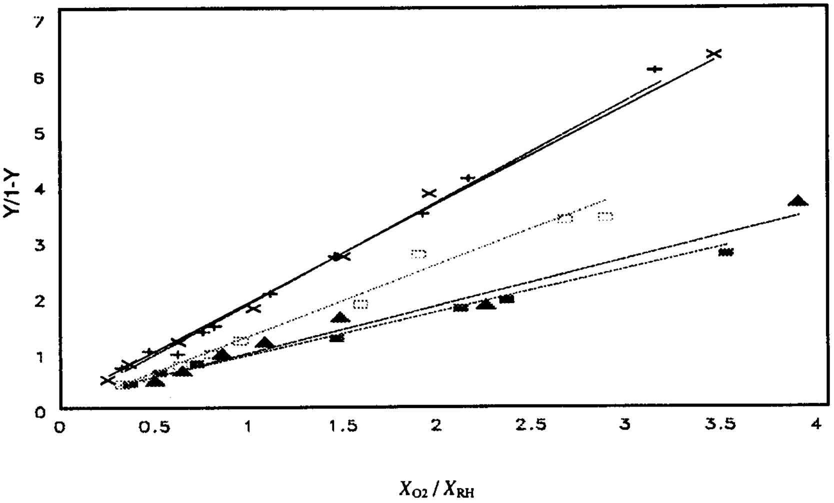


Figure 2a. Kinetic treatment of hot ^{11}CO yield data from alkene/oxygen systems buffered in xenon moderator where the slope equals $\sigma_{O2}\, I_{O2}/\sigma_{RH}\, I_{RH}$, (ethylene, ■ ; allene, + ; 1,3-butadiene, □ ; cis-2-butene, ▲ ; trans-2-butene, x).

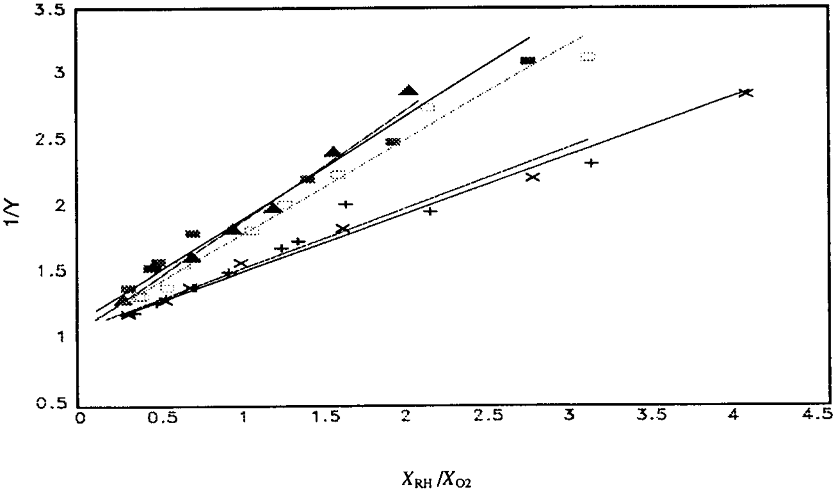


Figure 2b. Data contistency check and selection criteria for alkene/oxygen systems based on linearity and a constant intercept of α_{O2}/I_{O2}, (ethylene, ■ ; allene, + ; 1,3-butadiene, □ ; cis-2-butene, ▲ ; trans-2-butene, x).

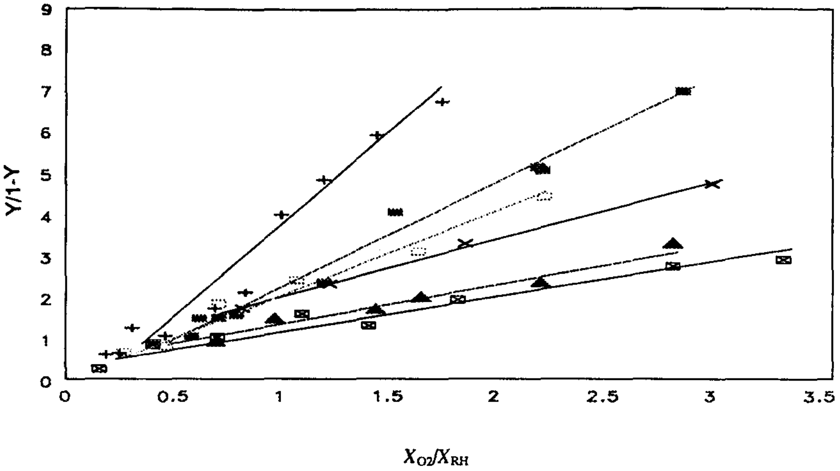


Figure 3a. Kinetic treatment of hot ^{11}CO yield data from aromatic/oxygen systems buffered in xenon moderator where the slope equals $\sigma_{O2}\, I_{O2}/\sigma_{RH}\, I_{RH}$, (benzene, □; toluene, + ; trifluorotoluene, ■; fluorobenzene, ▲ ; o-difluorobenzene, x; m-difluorobenzene, ⊠).

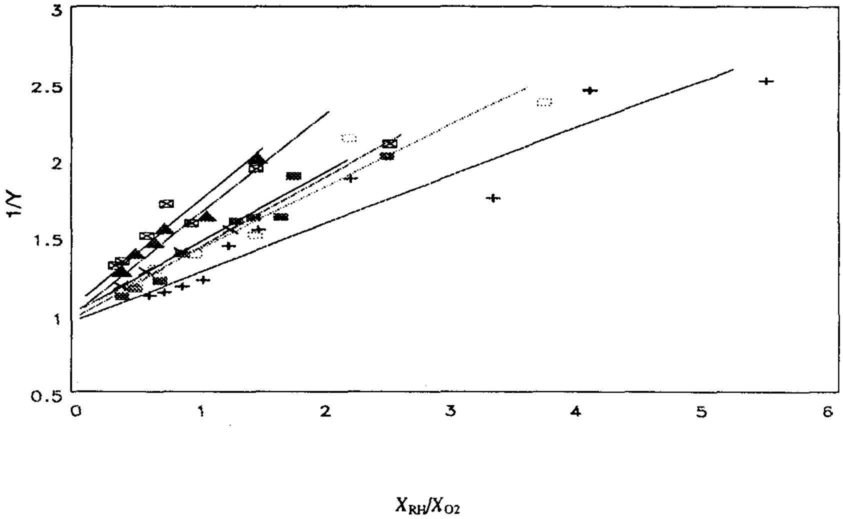


Figure 3b. Data consistency check and selection criteria for aromatic/oxygen systems based on linearity and a constant intercept of of α_{O2}/I_{O2} , (benzene, □; toluene, + ; trifluorotoluene, ■; fluorobenzene, ▲ ; o-difluorobenzene, x; m-difluorobenzene, ⊠).

of the power of equation 8 to exclude certain data points, based on our consistency test and selection criteria, we left in a few outlying points at high χ_{RH}/χ_{O_2} in Figure 1b for propane, butane and pentane. These points are obviously well off the linear plots depicted, and would definitely impact on the constancy of α_{O_2}/I_{O_2}.

Table 4

	Eq 10 Treatment	Eq 8 Treatment	
Hydrocarbons	$\sigma_{O_2}I_{O_2}/\sigma_{RH}I_{RH}$	α_{O_2}/I_{O_2}	Relative Reactivity
Methane	17.84 ± 1.26	1.03 ± 0.01	1.00
Ethane	10.41 ± 0.57	1.07 ± 0.04	1.71
Propane	10.63 ± 0.25	1.07 ± 0.08	1.68
n-Butane	4.76 ± 0.24	1.23 ± 0.13	3.75
n-Pentane	2.04 ± 0.07	1.42 ± 0.22	8.75
Ethylene	0.72 ± 0.01	1.23 ± 0.05	24.78
Allene	1.90 ± 0.04	1.04 ± 0.09	9.39
1,3-Butadiene	1.24 ± 0.06	1.07 ± 0.09	14.39
cis-2-Butene	0.88 ± 0.06	1.04 ± 0.07	20.27
trans-2-Butene	1.81 ± 0.04	1.07 ± 0.05	9.86
Benzene	2.48 ± 0.11	1.00 ± 0.07	7.19
Toluene	4.17 ± 0.31	1.03 ± 0.16	4.28
Trifluorotoluene	1.88 ± 0.14	1.09 ± 0.15	9.49
Fluorobenzene	1.02 ± 0.09	1.11 ± 0.06	17.49
o-difluorobenzene	1.38 ± 0.04	1.08 ± 0.01	12.93
m-difluorobenzene	0.79 ± 0.07	1.21 ± 0.13	22.58

We included in Table 4, column 3, the α_{O_2}/I_{O_2} values extracted from the equation 8 treatment of the yield data. In most cases reasonably good agreement in α_{O_2}/I_{O_2} was obtained for the data selected. Column 4 of the same table lists the calculated hydrocarbon reactivities relative to methane. These values were obtained by dividing the $\sigma_{O_2}I_{O_2}/\sigma_{RH}I_{RH}$ value for methane by the appropriate $\sigma_{O_2}I_{O_2}/\sigma_{RH}I_{RH}$ value for a particular hydrocarbon.

A key observation made within the saturated aliphatic hydrocarbon data set was that hydrocarbon reactivity tended to increase with the size of the carbon skeleton. The only anomally here was the observation that ethane and propane possessed essentially the same reactivity.

Another key observation made was that unsaturated aliphatic hydrocarbons were significantly more reactive toward ground-state carbon atoms than their saturated counterparts. For example, ethylene was 14.5 times more reactive than ethane. This increased reactivity can be attributed to the participation of the π-electrons as highly reactive sites for carbon atom reaction.

Interestingly, slightly larger alkenes were <u>less</u> reactive than ethylene. For example, trans-2-butene was 2.5 times less reactive than ethylene, although *cis*-2-butene was only 1.2 times less reactive. The difference in reactivity between the two isomers may be attributed, in part, to steric hindrance of the butene methyl groups thus inhibiting carbon atom attack at the π-bond. This suggests that ground-state carbon atoms attack the π-bond along the plane of the molecule, and not along the perpendicular plane set up by the π^*_y and π^*_z molecular orbitals. The influence of this steric effect might then be greater with the trans isomer since both sides of the molecule are blocked in this configuration. The overall lower reactivity of the butene molecules might also be due in part to the effect of back donation of electrons from the methyl groups onto the π–bond creating a net reduction in reactivity of that bond. This effect was also seen in our comparison of benzene and toluene reactivities to be discussed.

We also noted that aliphatic polyenes like allene and 1,3-butadiene were 2.6 and 1.7 times less reactive than ethylene, respectively. However, the decrease in π-bond reactivity here was most likely due to delocalization of the π-electrons through bond conjugation which had a net stabilizing effect.

Resonance stabilization carried to the extreme of aromatic behavior had the effect of decreasing π-bond reactivity even further. For example, benzene's reactivity of 7.2 was more like that of a saturated hydrocarbon of equivalent cross section than a polyene. Interestingly, electron donating groups on the aromatic ring decreased reactivity even further. We noted that toluene was 1.7 times less reactive than benzene with an overall reactivity of 4.3. This behavior supports an earlier hypothesis formulated on the mechanisms of reactions involving carbon-11 atoms and toluene[47], that primary reactions proceeded through ring C-H or side-chain C-H insertion, but not through π-bond interaction.

Contrary to this, electron withdrawing groups increased reactivity of the π-bonds in aromatic molecules. Reactivities were measured as 17.5 for fluorobenzene, 12.9 for o-difluorobenzene and 22.6 for m-difluorobenzene corresponding to increases in reactivity over benzene of 2.4, 1.8 and 3.1, respectively. Interestingly, two fluorine atoms affixed to the ring in the meta position had the effect of increasing the ring reactivity to a level almost equivalent to ethylene. Trifluorotoluene also had a reactivity of 9.5, corresponding to a 1.3-fold increase over benzene. Although not as drastic an effect as the fluorobenzenes, trifluorotoluene still fit the trend of behavior we observed for aromatic reactivity, that electron withdrawing substituents increased reactivity.

CONCLUSIONS

Interestingly, the trends exhibited in the present work are atypical of what one would expect from conventional electrophilic aromatic substitution reactions. Perhaps the closest analogies one could make with ground-state triplet carbon atom reactions are those reactions involving carbenes. Like carbon atoms, carbenes will undergo characteristic reactions such as insertions into aliphatic carbon-hydrogen bonds and additions to olefinic carbon-carbon double bonds.[58-63] However, unlike carbon atoms, carbenes will also undergo cycloaddition reactions with the double bonds of aromatics typically yielding ring expanded products.[64,65] However, our earlier work involving carbon-11 atom reactions with toluene[47] clearly showed from labelling distribution studies of key reaction products, that the double bonds of the aromatic substrate were not important sites for primary reaction.

This distinction in behavior becomes even more obvious in a comparison of results from the present work with those of an earlier study of Baldwin and Smith[66] involving thermally generated carbethoxy carbene, and its reactions with similar substituted benzenes. In this earlier work, relative rates of reaction were measured for the following compounds: anisole (1.15); toluene (1.06); benzene (1.00); fluorobenzene (0.80); chlorobenzene (0.84); and trifluorotoluene (0.55). From the observed substituent effects on aromatic reactivity, it was clear that this carbene was reacting in a manner characteristic of an electrophilic reagent.

Similar behavior can be seen between carbenes and alkyl substituted olefins[67] as well. Typically, chemical reactivity of olefins towards carbenes and other electrophiles increases as a function of the number of alkyl substituents, as well as a function of the nature of these substituents. However, our results showed just the opposite behavior, where olefin reactivity toward triplet carbon decreased with alkyl substitution on the carbon-carbon double bond.

These observations raise some interesting questions regarding just how triplet carbon atoms behave under certain reaction conditions. We can not argue that carbon atoms are electron deficient in nature. However, triplet carbon does not appear to behave like a typical electrophilic reagent when reacting with olefinic and aromatic substrates. Clearly, this point needs further investigation.

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56. Carbon-11 atoms may be generated from beam interaction with oxygen-16 in the quartz window through the $^{16}O(p,p\alpha n)^{11}C$ reaction. These atoms may then react with bond oxygen in the quartz matrix to yield $^{11}CO_2$. The amount of $^{11}CO_2$ released into the gas would then be dependent only on the applied irradiation dose and not the oxygen concentration in the gas.
57. The validity of this premise was tested in part (see reference 48) by monitoring the ^{11}C-to-^{11}CH distribution as a function of oxygen concentration. This was accomplished by comparing [^{11}C]-acetylene and [^{11}C]-ethylene yields which represent hot products from ^{11}C and ^{11}CH chemistry. This distribution remained constant in binary oxygen-alkane systems using ethane and propane, suggesting that molecular oxygen scavenging of ^{11}CH is not a dominant channel.
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