Reaction of Iron(II) Oxide with Alkenes at 77 K

GALO CARDENAS-TRIVINO*, PHILIP B. SHEVLIN**
Department of Chemistry, Auburn University, Auburn, Ala. 36849, U.S.A.
and KENNETH J. KLABUNDE**
Department of Chemistry, Kansas State University, Manhattan, Kans. 66506, U.S.A.

(Received October 10, 1986)

The reaction of iron atoms with ethylene and also the behavior of this matrix in the presence of other alkenes has been recently reported [1]. A brief study of the reactions of evaporated iron(II) oxide was conducted in order to correlate some results obtained in the reactions of the iron–ethylene matrix in the presence of oxygen [2]. Addition of oxygen to the Fe–C_2H_4 matrix generated ethane, n-butane, 1-butene, E- and Z-2-butene with predominant yield of butenes. On the other hand, addition of propylene to the Fe–C_2H_4 matrix followed by addition of oxygen also produced ethane, n-butane, 1-butene, E- and Z-2-butene in a similar yield as before.

Evidence for the existence of FeO has been given by Chang [3], who reported the synthesis of FeO by direct evaporation of iron at 850 °C and 10^{-7} torr. After preparing a film with a thickness of 100 Å, the film was exposed to water vapor. A layer of FeO was observed with 15% conversion.

Green *et al.* [4] have reported the IR spectrum of FeO as having a harmonic vibrational frequency at 880 cm^{-1}. They also showed bands for the isotopomers isolated in an Ar matrix at 14 K. These values are consistent with the assignment of the FeO vibration by Abramowitz *et al.* [5] and also with the values obtained from gas-phase electronic spectra [6], chemiluminescence and photoluminescence [7, 8].

Experimental

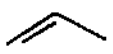
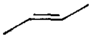
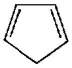
Iron(II) oxide (purchased from Alfa Products) was evaporated from a resistively heated crucible, as described for iron [1, 2] and cocondensed with ethylene. FeO and ethylene were cocondensed at 77 K for 30–60 min using 55 amperes and 10^{-3} mm of Hg. Alkene reactants were added following the cocondensation. After warming up the reactor for 1 h the products were pumped out through two traps at 146 and 77 K.

Gas chromatographic (GC) analysis of hydrocarbon products was carried out on a 20 ft dimethyl sulfolane column with a Carle microdetector. Infrared measurements were carried out on a Perkin-Elmer 983 Model spectrometer. Iron(II) oxide (1.25 mmol) and ethylene were cocondensed at 77 K. Styrene (8.7 mmol) dissolved in methylcyclohexane (3 ml) was added to the matrix at 77 K. The reactor was allowed to stand at room temperature with stirring overnight. The products were analyzed by GC with a 6 ft SE-30 column, between 35–220 °C (heating rate of 10 °C/min), using biphenyl as internal standard.

Results

In some cases alkenes were added to the matrix prior to warm up. Observed products and yields are summarized in Table I. In the reaction of FeO with ethylene alone or with ethylene after addition of propylene, small yields of butenes are formed (Table I). These butenes are probably formed by the

TABLE I. Reaction of Iron(II) Oxide with Ethylene and Alkenes

FeO	Reactants (mmol)			Products (mmol)						C_2H_4 [a]	Runs
	C_2H_4		Other								
1.22	10	1	–	7.1×10^{-2}	1.05	7.7×10^{-3}	6.3×10^{-2}	5.0×10^{-3}	2.2×10^{-3}	6.6	2
0.50	10	1	–	6.4×10^{-3}	1.06	9.2×10^{-3}	4.4×10^{-3}	2.6×10^{-3}	1.8×10^{-3}	7.9	1
1.48	10	–	–	–	–	3.6×10^{-2}	8.6×10^{-3}	9.4×10^{-3}	8.9×10^{-3}	6.0[b]	2
1.25	10	–	Ph–CH=CH_2 (8.70)	*trans*-stilbene (6.1×10^{-3}) + *cis*-stilbene (3.2×10^{-3})							3
1.02	–	–	 (30)	ferrocene (1.1×10^{-2})							2

[a] Ethylene recovered from the reaction.
[b] 5×10^{-2} mmols of ethane were obtained.

---

*On leave from Departamento de Quimica, Universidad de Concepcion, Casilla 3-C, Concepcion, Chile.

**Authors to whom correspondence should be addressed.

0020-1693/87/$3.50

ethylene dimerization reaction reported before [1]. It is interesting that iron oxide apparently is involved during the reaction.

Probably the most interesting result is the reaction with styrene where the formation of low yields of *trans*- and *cis*-stilbene in a ratio of 2:1 was observed.

When iron(II) oxide and cyclopentadiene were cocondensed at 77 K, ferrocene was obtained as the only product. Probably, iron oxide can abstract hydrogen from two molecules of the diene yielding ferrocene and water. It seems that the best evidence for FeO in the gas phase is the formation of stilbene.

A matrix isolation experiment was also carried out at 10 K. A pellet of FeO was made using a press at 2×10^4 psi. The sample was evaporated using an Excimer Laser Questec Series 2000 with a XeCl laser of 308 nm. The IR was recorded in a Beckman IR-2 Model. Ethylene (10% in Ar matrix, 400 microns of pressure) was reacted with FeO. After 4 h of reaction the IR spectrum was recorded and showed mainly free ethylene (3100, 2980, 2350, 1440 and 950 cm^{-1}), and a band of medium intensity at 880 cm^{-1} corresponding to FeO. After warming up to 20 K, the same IR spectra was obtained. Kafafi *et al.* [9] reported recently the FTIR spectrum of the iron atoms and dimers with ethylene between 13.5–15 K. Under our experimental conditions no bands for $Fe(C_2H_4)$, $Fe_2(C_2H_4)$ or $Fe_2(C_2H_4)_2$ complexes were found in the IR spectrum which might be evidence for the absence of Fe of Fe_2 species in the gas phase. There is also a possibility that a higher oxide might be formed during the codeposition. To verify their absence, Fe_2O_3 was cocondensed with ethylene at 77 K and after warming up there was no evidence of butenes by either GC or IR analysis.

Acknowledgements

The authors wish to thank the Petroleum Research Fund, administered by the American Chemical Society for financial support. We are grateful to G. H. Jeong for his assistance in the matrix isolation experiment.

References

1 G. Cardenas-Trivino and P. B. Shevlin, *J. Org. Chem., 49,* 4726 (1984).
2 G. Cardenas-Trivino, *Ph.D. Thesis,* Auburn University, March 1986.
3 S. Chang and W. H. Wade, *J. Colloid Interface Sci., 34* (3), 413 (1970).
4 J. Green, W. David and G. Reedy, *J. Mol. Spectrosc., 78,* 257 (1979).
5 S. Abramowitz, N. Acquista and I. W. Levin, *Chem. Phys. Lett., 50,* 423 (1977).
6 R. F. Barrow and M. Senior, *Nature (London), 223,* 1359 (1969).
7 A. B. Callear and R. G. W. Norrish, *Proc. R. Soc. London, Ser. A, 250,* 304 (1960).
8 A. M. Bass, N. A. Kuebler and L. S. Nelson, *J. Chem. Phys., 40,* 3121 (1964).
9 Z. H. Kafafi, R. H. Hauge and J. L. Margrave, *J. Am. Chem. Soc., 107,* 7550 (1985).