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(Polystyrylbipyridine)(tetracarbonyl)tungsten. An Active, Reusable Heterogeneous Catalyst for Metathesis of Internal Olefins

Seizo Tamagaki, Roger J. Card, and Douglas C. Neckers*

Contribution from the Department of Chemistry, Bowling Green State University, Bowling Green, Ohio 43403. Received December 1, 1977

Abstract: (Polystyrylbipyridine)(tetracarbonyl)tungsten is prepared from the reaction of polystyrylbipyridine and tungsten hexacarbonyl in refluxing xylene. This material is an active cocatalyst for the metathesis of internal olefins. Ethylaluminum dichloride is required as a cocatalyst. Greater than 90% conversion of 2-pentene to a 1:2:1 ratio of 2-butene, 2-pentene, and 3-hexene can be obtained in less than 40 min at room temperature. The catalyst can be easily recovered from the reaction solution and reused. Oxygen has a dramatic rate-increasing effect on the metathesis. The most effective catalysts have a W/bipyridine ratio close to unity. (Polystyrylbipyridine)(tetracarbonyl)molybdenum, (polystyryl(diphenylphosphine)(pentacarbonyl)tungsten, (bipyridine)(tetracarbonyl)tungsten, and (triphenylphosphine)(pentacarbonyl)tungsten were also prepared. The polymer bound catalysts are at least an order of magnitude more active than the analogous nonpolymer bound species. The tungsten compounds are more active than the molybdenum compound. And the polymer-bipyridine-tungsten system is more active than the polymer-phosphine-tungsten system.

Introduction

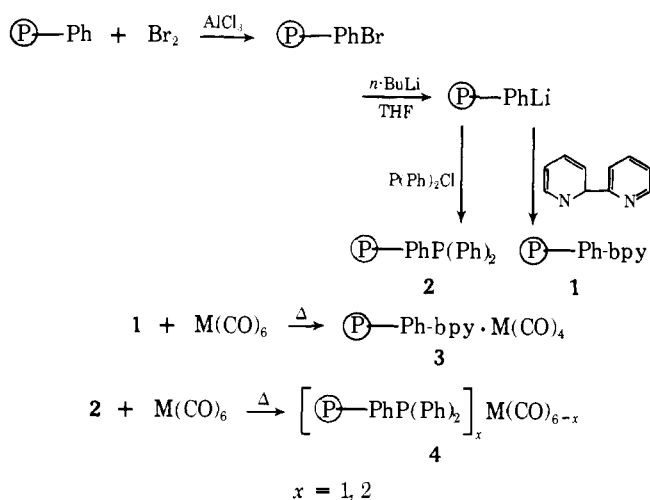
The pioneering work of Merrifield demonstrated many of the advantages inherent in the use of a polymer bound reagent in polypeptide synthesis.¹ Interest and activity in this area have grown dramatically over the past few years and immobilized enzymes, photosensitizers, organic reagents, and transition metal reagents and catalysts are frequently reported.²⁻⁴

Polymer based organotransition metal catalysts offer several significant advantages in synthetic and industrial chemistry,

Of these, the ease of purification of the reaction product(s) and the ease of recovery and reuse of the catalyst are most important. As part of our continuing interest in the development and use of polymer bound reagents,⁵⁻¹¹ we have reported that polystyrylbipyridine¹² is a generally useful support for the preparation of heterogeneous catalysts for such processes as the hydrogenation of alkenes and alkadienes^{13,14} and the isomerization of strained hydrocarbons.¹⁵ This report describes the use of polystyrylbipyridine in the preparation of a heterogeneous catalyst for olefin metathesis.

Since the initial report of olefin metathesis by Banks and

Scheme I



Bailey, many workers have studied its scope and mechanism.^{16,17} Complexes of the group 6 metals are among the most effective catalysts.¹⁶

In spite of considerable activity in this area, few successful polymer-based metathesis catalysts have been reported. Use of $\text{P-PhCH}_2\text{P(Ph)}_2\text{Mo(CO)}_5$ in the presence of ethylaluminum dichloride and oxygen results in slow metathesis of 2-pentene.¹⁸ Grubbs has reported the use of $\text{P-Sn(CH}_3)_3 + \text{WCl}_6$ for the metathesis of 1,7-octadiene.¹⁹ And Gassman and Chang have observed that materials obtained from the reaction of P-Ph-WCl_5 with lithium aluminum hydride readily catalyze the metathesis of 2-pentene.²⁰ This reaction is slightly slower than the reaction catalyzed by analogous nonpolymer bound system but results in a more stereoselective process.²⁰

In this report, we present the synthesis of two types of polymer-anchored tungsten and molybdenum catalysts and their use in the metathesis of internal olefins.

Results and Discussion

Preparation of Polymer Bound Catalysts. Polymer bound molybdenum and tungsten complexes were prepared from polystyrene-2%-divinylbenzene by application of established methods (Scheme I).^{12,21} In the case of **3** ($M = W$), the amount of metal incorporation was controlled by the amount of tungsten hexacarbonyl used. The color of the isolated polymer **3** varied from red to black with increasing loading of the metal. The infrared spectrum of **3** ($M = W$) contains bands at 2010, 1910, 1880, and 1830 cm^{-1} identical with that of (bipyridine)tetracarbonyltungsten.²²

The preparation and spectral data of the analogous molybdenum complex are similar.

Polymer **4** ($M = W$), a gray powder, was characterized by its IR spectrum which contains bands at 2060 (m), 1980 (w), and 1945 cm^{-1} (s, br), in close agreement with that of (triphenylphosphine)(pentacarbonyl)tungsten.²³ The lack of significant absorptions at ~ 1890 and ~ 2010 cm^{-1} demonstrates that disubstitution is very minor at best.^{23b} Data concerning elemental analysis are presented in the Experimental Section and appropriate tables.

Pittman has reported that the polymer-phosphine-tungsten complex, made from the interaction of $\text{P-PhCH}_2\text{PPh}_2$ (1% cross-linked) and tungsten hexacarbonyl contains IR bands at 2050 (m), 1975 (w), 1928 (s br), and 1880 cm^{-1} (sh).²⁴ The band observed at 1880 cm^{-1} could arise from the presence of some trans diphosphine tungsten complexes in his polymer. This should be facilitated by (1) the increased flexibility due to the lower cross-linking and the presence of the extra methylene group in Pittman's system, and (2) the higher phosphorus

Table I. The Effect of Catalyst on the Rate of Metathesis of 2-Pentene^a

catalyst	metal present			% conversion
	loading, mequiv/g resin	total mmol	time, min	
3 ($M = W$)	0.14	0.043	8 ± 2	25
4 ($M = W$)	0.17	0.043	13 ± 2	25
3 ($M = Mo$)	0.35	0.043	600	1
bpyW(CO) ₄		0.043	200	25
Ph ₃ W(CO) ₅		0.044	350	5
bpyMo(CO) ₄		0.043	no reaction	

^a The reaction was performed under argon at 25 °C. 2-Pentene (2.5 mmol) was added to the solution resulting from the interaction of the metal catalyst with 0.22 mmol of ethylaluminum dichloride in 10 mL of chlorobenzene.

loading ($\sim 3.8\%$) in Pittman's system as opposed to $<1\%$ in our polymer.

Olefin Metathesis. The metathesis of 2-pentene was conducted in the presence of catalysts generated in situ from the interaction of polymer-metal reagents **3** and **4** and ethylaluminum dichloride. Neither the polymer nor the aluminum reagent alone was sufficient to catalyze the reaction. In the standard procedure, ethylaluminum dichloride was added to a stirred suspension of **3** or **4** in chlorobenzene in an argon atmosphere. After 1 min, the 2-pentene was added all at once via syringe. Fractions were withdrawn periodically and examined by GLC.

In most cases, an initial rapid conversion to 2-butene and 3-hexene is observed, followed by a dramatically slower conversion. The formation of a 1:2:1 mixture of 2-butene, 2-pentene, and 3-hexene is defined as 100% conversion. The products were identified on the basis of spectral data.

A variety of catalysts were examined under similar reaction conditions (Table I). In every case, the polymer bound transition metal catalyst is at least an order of magnitude more active than the nonpolymer bound analogue. Tungsten catalysts are more reactive than the analogous molybdenum species in agreement with the findings of other workers,²⁵ and the bpy-tungsten systems are more reactive than the phosphine-tungsten systems under these conditions.

The use of (triphenylphosphine)(pentacarbonyl)tungsten and ethylaluminum dichloride for the in situ generation of an olefin metathesis catalyst has been reported by other workers.^{26,27} Romain and Trambouze demonstrated that bis(triphenylphosphine)(tetracarbonyl)tungsten was less reactive than the monophosphine complex.²⁶ Our observation of the greater reactivity of (bipyridine)(tetracarbonyl)tungsten relative to (triphenylphosphine)(pentacarbonyl)tungsten must be due either to the change from phosphorus to nitrogen ligands or to a difference of geometry of the two tetracarbonyl species. It is interesting that the difference in reactivity of the bipyridine and monophosphine systems is dramatically reduced upon polymer binding of the respective catalysts.

(Polystyrylbipyridine)(tetracarbonyl)tungsten is easily recovered after its use in metathesis by filtering the reaction solution through a fritted glass filter. It can be reused as a cocatalyst if the filtration is carried out under argon. The catalyst is not allowed to dry. Ethylaluminum dichloride must be added for each new reaction. The data in Table II demonstrate that there is some decrease in catalyst activity upon reuse. This may be due to small amounts of leaching of the metal or to a destruction of some "active sites". The reaction solution itself is not an active catalyst for metathesis, so leached metal must be present in inactive form.

Careful control of reaction conditions is required to obtain effective metathesis catalysis and the order of addition of re-

Table II. Activity of Reused (Polystyrylbipyridine)(tetracarbonyl)tungsten^a

use	T ₄₀ ^b	T ₆₀ ^b
1st	5 ± 2	8 ± 2
2nd	5 ± 2	30 ± 4
3rd	7 ± 2	22 ± 4
4th	40 ± 5	110 ± 15

^a The reactions were conducted under argon at 25 °C. 2-Pentene (2.5 mmol) was added to the solution resulting from the interaction of 400 mg (0.057 mmol W) of (polystyrylbipyridine)(tetracarbonyl)tungsten and 0.11 mmol of ethylaluminum dichloride. ^b T_n = the time required for n% conversion.

Table III. The Effect of the Quantity of Ethylaluminum Dichloride Used on the Metathesis of 2-Pentene^a

total EtAlCl ₂ , mmol	Al/W	T ₅₀	T ₆₀	T ₇₀
0.05	1.2	28 ± 3	48 ± 4	95 ± 7
0.11	2.5	22 ± 2	30 ± 2	48 ± 5
0.22	5.0	40 ± 3	85 ± 5	190 ± 15

^a 2-Pentene (2.5 mmol) was added to the solution resulting from the interaction of 300 mg (0.043 mmol W) of (polystyrylbipyridine)(tetracarbonyl)tungsten and ethylaluminum dichloride in chlorobenzene under argon.

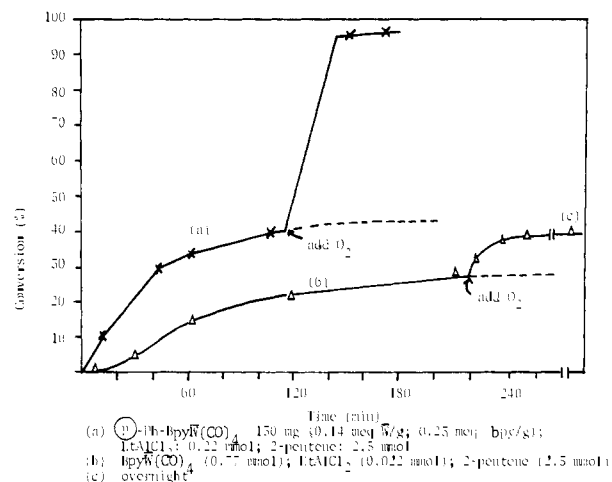
agents is important. If the 2-pentene is added before the ethylaluminum dichloride, competing reactions occur and very small amounts of metathesis products are observed. Under otherwise identical conditions, addition of ethylaluminum dichloride to (polystyrylbipyridine)(tetracarbonyl)tungsten followed by addition of 2-pentene resulted in quantitative conversion to metathesis products, whereas addition of 2-pentene prior to the addition of ethylaluminum dichloride resulted in 50% conversion to metathesis products. The balance of the pentene was converted to unidentified products.

The addition of oxygen has a dramatic effect on the metathesis of 2-pentene, especially in the case of the polymer-bound catalyst (Figure 1). In this case, 150 mg of (polystyrylbipyridine)(tetracarbonyl)tungsten (0.14 mequiv W/g; 0.23 mequiv bpy/g) was added as the catalyst. The reaction was allowed to proceed until a slow, steady conversion to metathesis products was observed. At this time, oxygen was bubbled into the solution. Within 30 min the conversion increased from 40 to <90%.

Table IV. The Effect of Tungsten and bpy Loading on the Metathesis of 2-Pentene

run ^a	polystyryl-bipyridine batch no. ^b	W loading, mequiv W/g	mg of polymer	mmol W	T ₂₀ , min ^c	T ₅₀	T ₇₀	T ₉₀
1	I	0.27	400	0.11	<5	8	10	36
2	I	0.27	100	0.03	≤5	18	35	95
3	I	0.23	400	0.09	8	95	196	
4	I	0.19	400	0.08	122	>300		
5	I	0.14	400	0.06	>>300			
6	II	0.16	400	0.06	<5	6	10	33
7	II	0.16	200	0.03	≤5	18	54	185
8	II	0.14	400	0.06	≤5	10	25	60
9	III	0.09	400	0.04	≤5	10	14	22
10	III	0.09	200	0.02	6	23	74	
11	III	0.07	400	0.03	7	34	98	220

^a The reactions were conducted under argon. 2-Pentene (2.5 mmol) was added to the solution resulting from the interaction of a polymer and 0.22 mmol of ethylaluminum dichloride in 10 mL of chlorobenzene. ^b These polymers contain decreasing amounts of bipyridine in the order I, II, III. Elemental analysis for nitrogen indicates 0.35 mmol of bpy/g I, 0.20 mmol of bpy/g II, and <0.1 mmol of bpy/g III. ^c The times listed are ±10%.

**Figure 1.** The effect of oxygen on the metathesis of 2-pentene.

Similar results have been observed by other workers for both polymer and nonpolymer bound systems.^{18,26,27} The results of Basset et al. have demonstrated that oxygen is most effective if added after the interaction of ethylaluminum dichloride and the metal cocatalyst.²⁷ And, consistent with the findings of other workers,²⁷ the amount of ethylaluminum dichloride added is also important. As demonstrated by the data in Table III, the addition of either too much or too little ethylaluminum dichloride results in decreased catalyst efficiency.

The data in Table IV illustrate the effect of altering the tungsten and bipyridine loading of the polymer. From these data, it is apparent that the most important factor in catalytic efficiency is that the ratio of tungsten to bipyridine be as close to unity as possible. The catalysts in runs 1, 6, and 9 are all very active catalysts in spite of the fact that the total amount of tungsten present decreases from 0.11 to 0.04 mmol in this series.

The data from runs 1, 3, 4, and 5 show significant decrease in reactivity as the ratio of bpy to tungsten increases. That this is not due to the decreased amount of tungsten is obvious from the data discussed above and by a comparison of runs 3–5 with run 2. In spite of a threefold increase in tungsten present, run 3 is much slower than run 2. The comparison of runs 6–8 and runs 9–11 shows the same effects. Maximum catalyst efficiency is observed when the ratio of tungsten to bipyridyl residues approaches unity. This could be due to inhibition of the catalytic process by uncomplexed bipyridine residues.

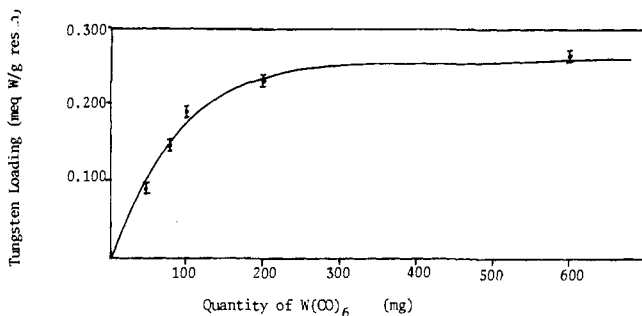


Figure 2. The effect of the amount of hexacarbonyltungsten on the metal loading.

Interestingly, polystyrylbipyridine does inhibit the otherwise normal metathesis of 2-pentene catalyzed by the polymer based tungsten reagent. In one example, the addition of 200 mg of polystyrylbipyridine (0.23 mequiv of bpy/g) to the metathesis of 2-pentene catalyzed by (polystyrylbipyridine)-(tetracarbonyl)tungsten results in a rate decrease from ~20% conversion after 140 min to ~10% conversion after 280 min. The addition of polystyrene instead of the polystyrylbipyridine has no significant effect on the rate of metathesis. This inhibition is probably the result of deactivation of the ethylaluminum dichloride on complexation to the bipyridine residues.²⁹ This complexation should be rapid under these reaction conditions.

It is not likely that the inhibition results from the interaction of the bipyridine residues with (bipyridine)(tetracarbonyl)tungsten. Formation of (polystyrylbipyridine)(bipyridine)(dicarbonyl)tungsten is not reasonable under these conditions,²² and formation of (polystyrylbipyridine)(tetracarbonyl)tungsten both is unlikely and would be expected to result in a rate increase rather than the decrease in rate observed.

The lack of observation of a rate increase on the addition of polystyrene or polystyrylbipyridine to this reaction also provides evidence that oxygen is not trapped in the polymer to a sufficient extent to explain the rate increase observed for the polymer bound catalysts as opposed to the nonpolymer bound analogues.

The metathesis of 2-heptene proceeds under similar condition at the same rate as that of 2-pentene within experimental error. Neither the metathesis of 1-(*p*-methoxyphenyl)-1-propene nor its cross-metathesis with 2-pentene is observed. Less than 20% conversion of 2-pentene is observed after 2 h under these conditions. 1-Octene does not undergo metathesis but does not interfere significantly with the metathesis of 2-pentene. Under conditions where the metathesis of 2-pentene had T_{20} and T_{45} of $12 \pm$ and 210 ± 25 min, the metathesis of 2-pentene in the presence of 1-octene was characterized by T_{20} and T_{45} of 50 ± 5 and 170 ± 20 min, respectively. No cross-metathesis products were observed.

In conclusion, we have described the preparation and use of the polymer bound metathesis catalysts made from P-Ph-bpy . In the case studied, the polymer bound catalysts are an order of magnitude more reactive than the analogous nonpolymer bound systems. The catalyst **3** ($M = W$) is more active than **4** ($M = W$). This trend is also observed in the nonpolymer systems and must be due to the presence of the cis chelating bipyridine ligand. The best catalyst, (polystyrylbipyridine)-(tetracarbonyl)tungsten, can be easily recovered from the reaction solution and may be reused. Although all reaction conditions are important, the W/bipyridine ratio is especially important. The most active catalysts are obtained when this ratio is close to unity.

Experimental Section

Proton magnetic resonance spectra were obtained on either a Varian

Associates CFT-20 or A-60 nuclear magnetic resonance spectrometer; infrared spectra on a Perkin-Elmer 337 grating infrared spectrophotometer; and GLC analysis on a Hewlett-Packard 5710 A gas chromatograph with flame ionization detectors and an Omniscrite recorder with disc integration. Elemental analyses of solid samples were performed by Spang Microanalytical Laboratory.

Analytical grade chlorobenzene was distilled twice from phosphorus pentoxide under nitrogen, stoppered with a septum, and stored under nitrogen. Reagent grade *o*-xylene and toluene were distilled from metallic sodium. Reagent grade tungsten and molybdenum hexacarbonyls were purchased from Apachi Chemical Co., and used without further purification. The alkanes and alkenes used were distilled over sodium and stored under nitrogen before use.

Polystyrylbipyridine was prepared from polystyrene-2% divinylbenzene as described previously.¹³ The resulting polymer was washed in refluxing aqueous THF, THF, chloroform, benzene, and hexane before use. Different bipyridine loadings were obtained by varying the amount of bipyridine used.

(Polystyryl)(diphenyl)phosphine was prepared by the method of Collman,²¹ from brominated polystyrene-2% divinylbenzene. The resin was washed as described above.

(Bipyridine)(tetracarbonyl)tungsten was prepared from the reaction of equimolar quantities of bipyridine and hexacarbonyltungsten in refluxing *o*-xylene according to the method of Stoddard:²² IR (HCCl_3 , cm^{-1}) 2010 (m), 1900 (s), 1075 (m), 1830 (m) (lit.²² 2008 (m), 1900 (vs), 1880 (sh), 1829 (s)).

(Bipyridine)(tetracarbonyl)molybdenum was prepared from the reaction of equimolar quantities of bipyridine and hexacarbonylmolybdenum in refluxing toluene according to the method of Stoddard:²² IR (HCCl_3 , cm^{-1}) 2010 (m), 1910 (s), 1880 (m), 1830 (m) (lit.²² 2014 (m), 1911 (vs), 1882 (sh), 1830 (s)).

(Triphenylphosphine)(pentacarbonyl)tungsten was prepared by the procedure of Magee et al.:^{23a} IR (HCCl_3 , cm^{-1}) 2080 (sh), 1990 (m), 1945 (s) (lit.²³ 2075 (w), 1980 (w), 1938 (vs)); mp $144\text{--}145^\circ\text{C}$ (lit.^{23a} 149°C).

(Polystyrylbipyridine)(tetracarbonyl)tungsten. In a typical procedure, 1.000 g of polystyrylbipyridine (0.34 mmol of bpy) and 600 mg (1.7 mmol) of hexacarbonyltungsten were allowed to react in refluxing *o*-xylene for 3 h in a nitrogen atmosphere. The resulting polymer was isolated by filtration through weighed frittered glass, and thoroughly washed with *o*-xylene, CHCl_3 , benzene, and *n*-hexane. The dark red polymer was dried in a vacuum oven at 50°C for 12 h, affording an increase in weight of the polymer (1.0862 g), which corresponds to tungsten loading of 0.268 mmol/g of polymer. The IR spectrum includes bands at 2010 (m), 1900 (vs), 1875 (vs), and 1835 cm^{-1} (s) in KBr very similar to that of (bipyridine)(tetracarbonyl)tungsten.²²

The procedure was repeated using smaller amounts of hexacarbonyltungsten to prepare samples with lower tungsten loading. The data correlating the amount of tungsten used and the final tungsten incorporation are presented in Figure 2. Similar methods were used for the preparation of the other polymers listed in Table IV.

(Polystyrylbipyridine)(tetracarbonyl)molybdenum. According to the above procedure, 1.000 g of polystyrylbipyridine (0.17 mmol of bipyridine) in 600 mg (2.3 mmol) of molybdenum hexacarbonyl were allowed to react in toluene at reflux for 3 h under nitrogen. The mixture was then cooled, washed with several solvents, and dried overnight at 50°C , giving 1.0537 g of the metalated red polymer beads (0.250 mmol/g of polymer): IR 2010 (m), 1905 (vs), 1880 (vs), 1830 cm^{-1} (s) in KBr, similar to that of (bipyridine)tetracarbonylmolybdenum.²²

(Polystyryl)(diphenylphosphine)(pentacarbonyl)tungsten was prepared from polystyryldiphenylphosphine and hexacarbonyltungsten in a manner analogous to that reported by Magee et al.:^{23a} IR (KBr, cm^{-1}) 2060 (m), 1980 (w), and 1945 (s, br), similar to that of the nonpolymer bound analogue.²³

Kinetics. Kinetics of metathesis of 2-pentene were performed at ambient temperature in a 25-mL one-necked round-bottom flask. The catalyst and a clean magnetic stir bar were added and then the flask was equipped with a septum. The air in the vessel was expelled by fast argon flow for 10 min through two syringe needles before 10 mL of chlorobenzene was added through a needle. In order to expel traces of air in the polymer and solvent, argon was bubbled into the solution for an additional 1 min. Ethylaluminum dichloride (0.22 mmol) was then added. One minute later, the reaction was started by introducing 2-pentene (2.5 mmol). The reaction was followed by using a $2\text{ m} \times \frac{1}{4}$ in. column packed with 10% Apieson L on Chromosorb W (60-80

mesh). The conversion percent was calculated from appearance of 3-hexene and disappearance of 2-pentene. Heptane was used as an internal standard.

Identification of Metathesis Products. A solution of 100 mg of $\text{bpyW}(\text{CO})_4$ or 1.5 g of the corresponding polymer-bound catalyst in 20 mL of chlorobenzene was treated with 0.75 mL of ethylaluminum dichloride under an argon atmosphere and then 4 mL of 2-pentene was added. After 2 h, the reaction mixture was worked up with water, filtered, dried over MgSO_4 , and then fractionally distilled. Identification of 3-hexene was made by comparing its IR, NMR, and mass spectra with those of the authentic material after fractional distillation (45–68 °C) of the product. Identification of 2-butene was made using a fraction (bp 25–40 °C) which also contained the starting 2-pentene.

Acknowledgment. This work was supported, in part, by the National Science Foundation (CHE-7610893) and the donors of the Petroleum Research Fund, administered by the American Chemical Society. Grateful acknowledgment is made to the donors of these funds.

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Hydrogen Rearrangements of Gaseous Butanoic Acid Cations

D. J. McAdoo,*^{1a} D. N. Witiak,^{1a} F. W. McLafferty,*^{1b} and J. D. Dill^{1b}

Contribution from The Marine Biomedical Institute, The University of Texas Medical Center, Galveston, Texas 77550, and the Department of Chemistry, Cornell University, Ithaca, New York 14853. Received December 27, 1977

Abstract: The principal pathways for the decomposition of butanoic acid ions (**1**) involve losses of C_2H_4 and CH_3 . Approximately 5% of the C_2H_4 loss involves the $\alpha\text{-CH}_2$ group, consistent with competitive isomerization to a cyclobutanediol intermediate. The loss of $\gamma\text{-CH}_3$ to form protonated acrylic acid occurs through two pathways; in addition to the one involving initial $\beta\text{-H}$ rearrangement, a second path favored for metastable **1** ions proceeds through direct $\alpha\text{-H}$ transfer to the carbonyl group. In contrast to the C_2H_4 loss, this CH_3 loss is accompanied by little H/D scrambling, and appears to arise from an *isolated electronic state* of **1**; this could be the π -ionized state, with $\alpha\text{-H}$ transfer to the carbonyl oxygen occurring through a suprafacial [1,3] sigmatropic shift. Such metastable **1** ions also appear to form ($\text{M} - \text{CH}_3$)⁺ ions through loss of ($\alpha\text{-CH}_2 + \beta\text{-H}$). In the decompositions of higher energy **1** ions hydrogen transfers through five- and three-membered ring intermediates are competitive with the six-membered counterpart; this indicates for the classical $\gamma\text{-H}$ rearrangement/olefin loss reaction that it is the β -cleavage step, not the $\gamma\text{-H}$ transfer, whose favorability leads to the characteristically high abundance of such reaction products in mass spectra.

One of the first studies of mass spectral reactions utilizing isotopic labeling was that of butanoic acid by Happ and Stewart.^{2a} Carbon-13 substitution showed that the unusual *m/e* 60 ion (**1**) from this compound had retained the carboxyl carbon; this ion is now understood to be formed by the ubiquitous reaction involving γ -hydrogen rearrangement and β -

cleavage,^{2b} **1** \rightarrow **3** (see Scheme I). Like its photochemical analogue, the Norrish type II rearrangement,³ this reaction appears to be stepwise in nature; based on decompositions of metastable **1-O-d**₁ and **1- γ -d**₃ ions,⁴ the exchange of β -, γ -, and O-hydrogen atoms prior to decomposition was postulated, **1** \rightleftharpoons **2** \rightleftharpoons **1a** \rightleftharpoons **2a** \rightarrow **3a** and **1** \rightleftharpoons **4** \rightleftharpoons **1b** \rightleftharpoons **2b** \rightarrow **3b**. Recent